STATUS REPORTS

to the

RECYCLED PAPER

AND

SURFACE AND COLLOID SCIENCE

PROJECT ADVISORY COMMITTEE

March 22 - 23, 1995

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

ANNUAL RESEARCH REVIEW

RECYCLED PAPER

AND

SURFACE AND COLLOID SCIENCE

March 22 - 23, 1995

February 15, 1995

TO: MEMBERS OF THE RECYCLED PAPER AND SURFACE AND COLLOID SCIENCE PROJECT ADVISORY COMMITTEES

Attached for your review are the Status Reports for the projects to be discussed at the Recycled Paper and Surface Colloid Science Project Advisory Committee meeting. The program review is scheduled for Wednesday, March 22, 1995, at 1:00 - 5:00 p.m. The Recycled Paper and Surface Colloid Science PAC committee meeting will meet on Thursday, March 23, 1995, from 8:00 a.m. to 12:00 p.m.

We look forward to seeing you at this time.

Sincerely,

David I. Orloff, Ph.D.
Professor of Engineering & Director
Engineering and Paper Materials Division

DIO/map

Attachments

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RECYCLED & SURFACE AND COLLOID SCIENCE PROJECT ADVISORY COMMITTEE MEETING

March 22-23, 1995
Institute of Paper Science and Technology
Atlanta, Georgia

AGENDA

Recycled Paper and Surface and Colloid Science (APR)

March 22, 1995

1:00 p.m. - 1:15 p.m.	Opening Remarks and Anti Trust Statement	Bob Moran
1:15 p.m. - 1:30 p.m.	Overview of Recycle Research	David Orloff
1:30 p.m. - 2:15 p.m.	Project F009-02 Interaction of Polyvinyl Acetate with Fiber	Sujit Banerjee
2:15 p.m. - 3:15 p.m.	Project F009-01 Improved Performance of Recycled Fines	John Waterhouse
3:15 p.m. - 3:30 p.m.	Break	
3:30 p.m. - 4:00 p.m.	Project F009-03 Multiphase Flow in Recycling Operations	Ted Heindel
4:00 p.m. - 5:00 p.m.	Project E00105 Strength Properties of Recycled Fibers and Paper	Richard Ellis

March 23, 1995

8:00 a.m. - 12:00 p.m.	Paper Physics Committee Discussions	David Orloff

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UTILIZATION OF RECYCLED FIBERS

STATUS REPORT

FOR

PROJECT F009

March 22 - 23, 1995

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

INTERACTION OF POLYVINYL ACETATE WITH FIBER

STATUS REPORT

FOR

PROJECT F009-02

Sujit Banerjee
Marshall Hutten
Charles Jeffrey
Mary Roberts

March 22 - 23, 1995

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

INTERACTION OF POLYVINYL ACETATE WITH FIBER

Project Title: RECYCLE

Project Staff: Marshall Hutten, Charles Jeffrey, Mary Roberts, Sujit Banerjee

Budget (FY94-95): $100,000

Reporting Period: FY94-95

Division: Engineering and Paper Materials

Project Code: RECYC

Project No. F00902

Introduction

The presence of stickies in recycled fiber can cause runnability problems, lead to hole and spot formation, and to decreased lifetime of felts. Industry attention has been focused on practical aspects of stickie prevention and removal, e.g., through more frequent pulper cleaning, and optimization of screens and slots and centricleaner efficiency. The approach described here is longer term and more fundamental in nature. It seeks to understand the chemistry of the interaction between pulp, water, stickie and surfactants using polyvinyl acetate (PVAc) as a model, and to then apply the principles developed toward the control of stickies. In particular, it targets methods to study and understand the distribution of stickies between water and fiber as a function of the various physicochemical conditions that exist in a mill. The intent is to use the information to direct the stickie into fiber or water for optimal removal.

Experimental Methods for the Britt Jar

In the previous year we devised a gravimetric method for determining fiber:water distribution. Briefly, a handsheet was prepared on a Formette Dynamique handsheet former. The instrument produces a very uniform handsheet to the point where a constant area of handsheet consistently represents a constant mass. Test strips from the Formette Dynamique were soaked for 30 seconds and then agitated at 800 rpm in the Britt jar. The agitator was situated just above the 200 mesh screen. After the agitator was turned on, the surfactant (if any) was first added and then the stickie solution or suspension was slowly introduced with a syringe. The system was maintained for 30 minutes with continuous agitation, after which the water was drained and collected. The volume of water was measured, and an aliquot was dried overnight. The fiber solids retained on the 200 mesh screen were also carefully collected and dried overnight. The results from a typical experiment using polyvinyl acetate (PVAc) are as follows. The distribution coefficient (K_d) is

solids in (g)			solids out (g)			error (g)
fiber	PVAc	total	fiber	water	total	
1.5308	0.1000	1.6308	1.5077	0.1141	1.6218	0.01
1.5308	0.0000	1.5308	1.4973	0.0206	1.5179	0.0129
PVAc balance:			0.0104	0.0935	0.1039	-0.0039

defined as the concentration of stickie in the fiber to that in water, i.e.

$$K_d = (m_{mat} - m'_{mat})/(m_{water} - m'_{water}) \quad (1)$$

where m_{mat} and m'_{mat} are the masses in the solid phase with and without the stickie respectively, and m_{water} and m'_{water} are the corresponding weights in the filtrate. All K_d values reported here were averaged from at least two values, and usually from three to four determinations.

Effect of Kappa Number and Surfactant Concentration on K_d

Distribution coefficients (K_d) were measured for a variety of softwood Kraft pulps, both with and without the presence of a surfactant. The surfactant in question was Lionsurf, a non-ionic surfactant used as a collector in de-inking. The results are illustrated in Figure 1. Our first conclusion is that K_d changes linearly with kappa number. Hence, under our conditions, PVAc will associate more strongly with brown pulp than with bleached. The second finding is that the surfactant has an inconsistent effect on K_d. The effect for the lower kappa pulps is quite small. However, K_d for the kappa 81 pulp drops steeply at the highest surfactant concentration. This result does not appear to be an artifact, since it occurred reproducibly. We plan to revisit the issue in the 95/96 cycle as a part of a broader study on surfactant effects on K_d.

Stability of Stickies on Fiber

In order to determine the strength of the stickie-pulp association, pulp was saturated with PVAc in methanol and dried. This pulp was then blended in different ratios with untreated pulp. Our reasoning was that if the stickie dissociated easily from the pulp during repulping, the stickie in the filtrate would increase in proportion to treated pulp in the mixture. On the other hand, if the stickie was principally retained by the fiber, then the stickie content of the mat would increase as the proportion of treated pulp used increased. The results shown in Table 1 clearly indicate that

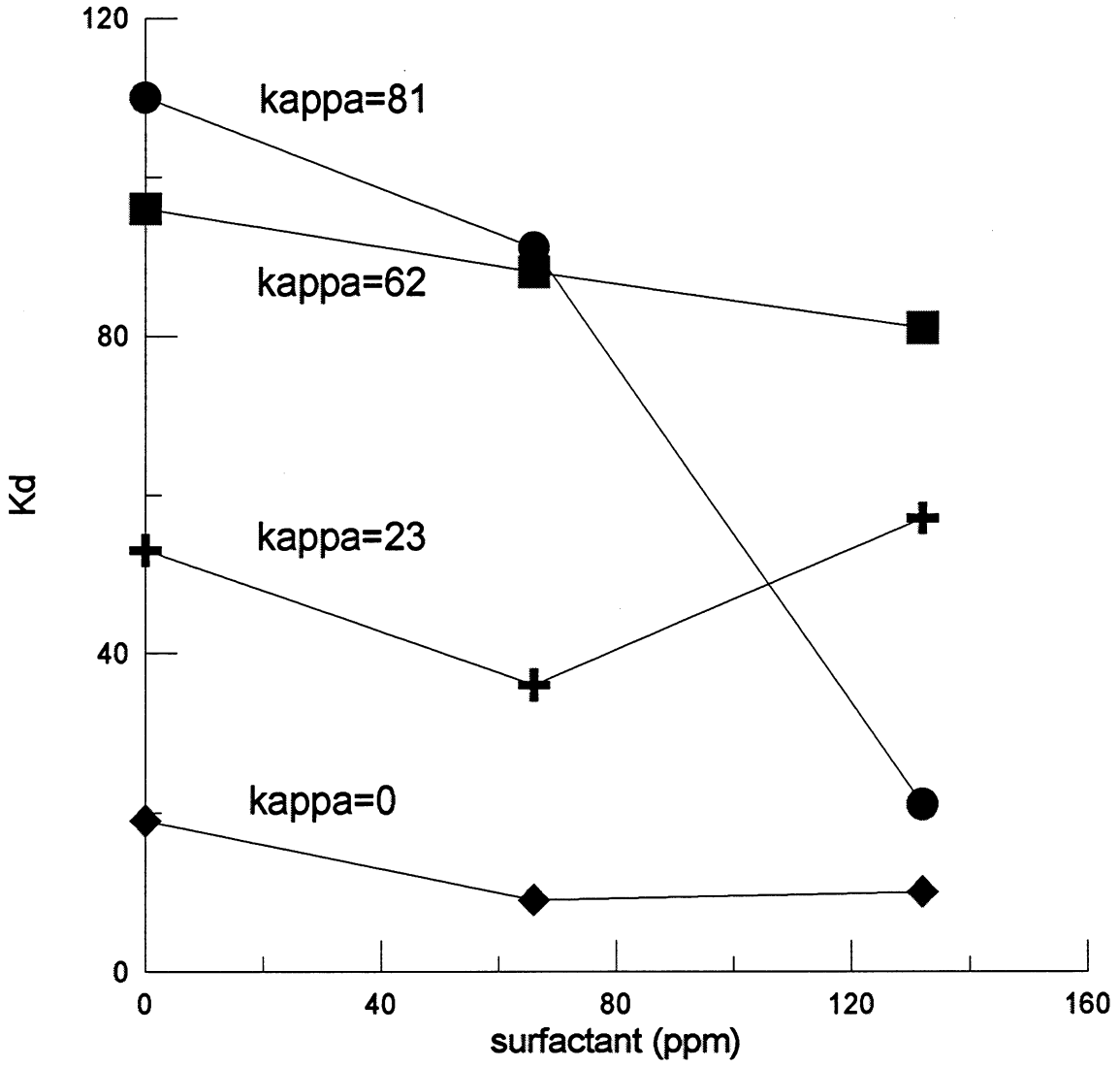


Figure 1. Effect of kappa number and surfactant concentration on K_d

PVAc in the mat is proportional to the amount of treated pulp in the system, indicating that once attached, the PVAc is not dislodged from the pulp under our conditions.

Table 1: Stability of Stickies on Fiber		
Percent treated pulp	**PVAc in mat (g)**	**PVAc in water (g)**
50	0.2	0.038
80	0.4	0.01
100	0.64	0.035

Effect of Retention Systems on K_d

Since retention systems reduce the fraction of fines in the system, the effect of retention systems on K_d would reflect the amount of stickies associated with the fines. The following retention system was used: anionic colloidal silica (0.06 g); cationic starch (0.06 g); alum (0.03 g.); fiber (3 g); resin (0.15 g); water (600 mL). Three types of PVAc were used, and for each, parallel experiments were done with and without the starch. The results shown below illustrate the dramatic

resin: 2873 flexible cross-linking PVAc latex for PSA (T_g=-36)
without starch: K_d=62; with starch: K_d=1,630 (355-3400)

resin: 1105 rigid PVAc latex for paper coating (T_g=29)
without starch: K_d=66; with starch: K_d=690 (235-1060)

resin: 9003-20-7 PVAc homopolymer, (T_g=29)
without starch: K_d=33; with starch: K_d=380 (210-480)

effect of the retention aid. The variability of the retention aid measurements is high because very little material remained in the filtrate and weight measurements were quite difficult. However, it is clear that a substantial amount of PVAc is associated with fines. The results in the next section will demonstrate that virtually all the PVAc recovered in the filtrate is associated with fines.

Effect of Freeness on K_d

In principle, the PVAc can be associated with fines or be freely suspended in water, and in order to distinguish between the two, we studied the effect of fiber length on K_d. Bleached pulp was beaten to different freeness levels and K_d measurements were made with each furnish. The results illustrated in Figure 2 demonstrate that K_d is inversely proportional to freeness.

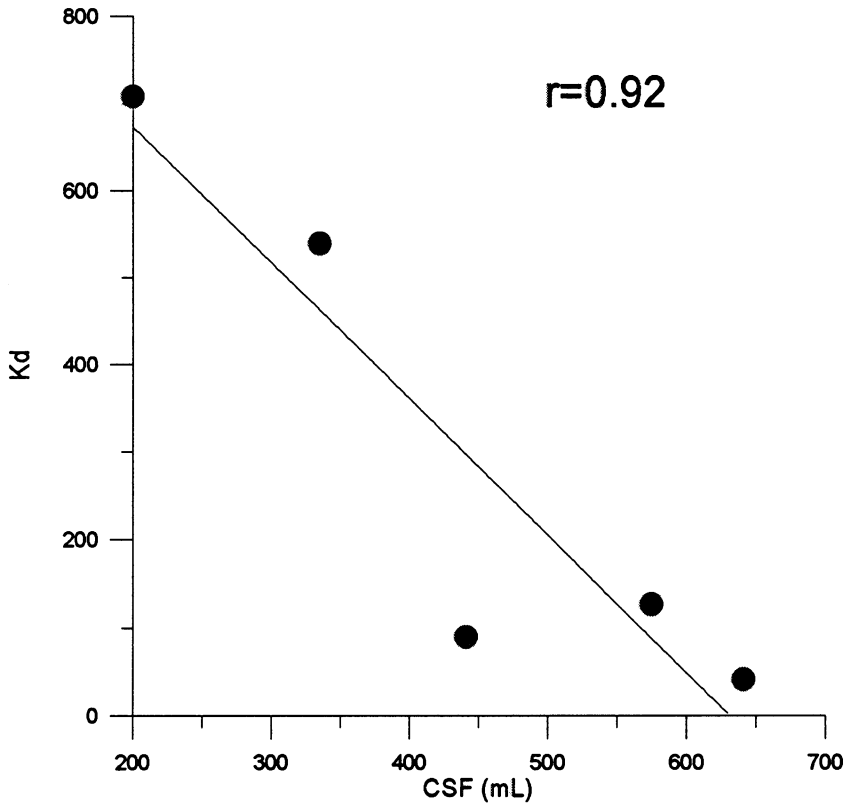


Figure 2. Dependence of K_d on freeness

The root cause of this dependence can be appreciated from the data presented below. The "fines in water" column measures the fines in the filtrate *without* the PVAc, i.e. it represents m'_{water} in eq (1). The "PVAc in water" represents the PVAc in the filtrate; i.e. it reflects (m_{water}-m'_{water}) in eq. 1.

freeness	fines in water (g)	PVAc in water (g)	PVAc/fines
641	0.0854	0.2093	2.45
575	0.0403	0.1447	3.59
441	0.0285	0.1489	5.22
335	0.0264	0.0901	3.45
200	0.0202	0.0612	3.03

The final column is the mass ratio of PVAc in the filtrate to that of fiber in the filtrate. The relative constancy of this ratio forces the conclusions that there is little or no free PVAc in the filtrate, and virtually all of it is tied up with the fines. We emphasize that this is true only under our conditions. Measurements at higher temperature and in the presence of surfactants are planned.

Preliminary Results on the Effect of pH on K_d

The effect of pH on bleached pulp was measured at three pH values as shown below. Inasmuch as these measurements have not been replicated, discussion is deferred until the results are confirmed. For the present, pH appears to have a significant effect on K_d. The negative value at pH 4 may either be real or may result from experimental error. A negative K_d implies (from eq. 1) that there is less solid material in the filtrate with the stickie added than without the stickie. At this stage, we place no significance to the apparently negative number.

pH	K_d
4	-20
7	67
9	80

Studies with the Formette Dynamique Sheet Former

The objectives of this phase of the work were to (a) demonstrate a Formette Dynamique handsheet procedure that will allow for the study of stickies distribution consistent with realistic paper machine process conditions, and (b) develop the procedure so that it can be used to address recycle paper mill operating problems.

In order to determine whether the conclusions reached with the Britt Jar experiments applied to more realistic systems, studies on stickie:water interactions were extended to the Formette Dynamique handsheet maker. The Formette Dynamique is a centrifugal handsheet former that has the following advantages for this type of study:

1. It produces handsheets with controlled MD:CD fiber orientation and other properties similar to paper produced on a paper machine.
2. The process parallels are the same, i.e. a process move made on the Formette will have the same directional effect as that made on a paper machine.
3. The white water and associated fines can be recycled into the next handsheet, thus simulating a paper machine fan pump loop. They can also be easily sampled.

4. The Formette has an inherent centrifugal effect that separates white water fines into heavy ("heavies") and light ("lights") fractions allowing separate studies of each of these fractions.
5. The Formette is capable of forming webs from a wide variety of materials including long synthetic fibers and particulate matter.
6. Formette handsheets are 8.5" x 35", providing ample material for testing.
7. Peel off from blotters, after handsheets are formed, provide a way of measuring stickiness.

Experimental Procedures for the Formette Dynamique

The Formette Dynamique forms handsheets by spraying the stock on to a moving forming fabric that lines the foraminous inside wall of a centrifuge bowl (see Figure 3). Bowl speed regulation controls MD:CD fiber orientation much like the drag on a paper machine. The white water passing through the forming fabric and inside support wall enters an annular space between the inner wall and an outer solid wall. Centrifugal force deposits heavy fines on the outer wall of the Formette. Light fines that are either colloidal in nature or lower in density than water exits with the white water at the bottom of the bowl. The white water under centrifugal gravity exits over a radial weir at the bottom of the bowl. The radial height of the weir fixes the water level or water wall over the forming fabric. The stock spray does not strike the forming fabric directly, but rather, the water wall covering the forming fabric.

Experiments were conducted with two wood pulps. One was a bleached softwood kraft market pulp; the other was an unbleached, never dried, softwood kraft obtained from a linerboard pulp mill (Kappa number = 62). Two series of six handsheets were made from each pulp: one with PVAc and the other without. For each series the white water collected from each handsheet was recycled for making the

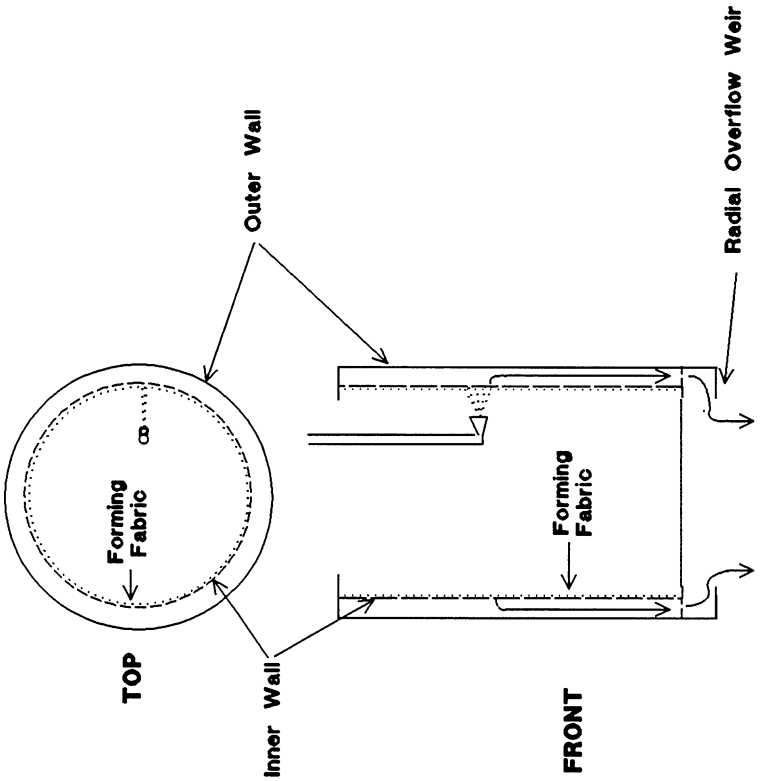


Figure 3
FORMETTE DYNAMIQUE

number = 62). Two series of six handsheets were made from each pulp: one with PVAc and the other without. For each series the white water collected from each handsheet was recycled for making the next handsheet. This included the water to dilute the stock to 0.5% consistency and also the water to build the water wall over the forming fabric.

The stock was prepared in a 5-lb. valley beater to approximately 1.8% consistency prior to dilution. It was beaten to 500 ml, Canadian Standard Freeness. A measured aliquot, enough for a 42 lb. handsheet, was withdrawn and diluted to 0.5% consistency in the 20-liter mix vessel that is part of the Formette apparatus. It was at this point that the PVAc contaminant was introduced as a 3% solution in methanol. The amount of bone-dry PVAc was based on it being 6% of the bone dry fiber.

The white water from each handsheet was collected, measured, and sampled for solids content. The solids in the white water are the "lights". After each series of six handsheets, the inner bowl of the centrifuge was removed and the "heavies" that collected on the outer wall were collected, dried and weighed. Each handsheet was removed from the forming fabric, weighed, wet pressed (50 psi for % minutes), dried under restraint on a drum dryer, and weighed again. When wet pressed and dried, the handsheets were sandwiched between blotters.

Results from Formette Dynamique Measurements

Material balance results based on 100 gm of bone-dry fiber are presented in Table 2. This represents the cumulative material balance for the six handsheets in each series. For each pulp, comparison is made to the series without PVAc contamination. This comparison allows for a determination of where

Table 2: Recycle Experiments Material Balance Comparison

Basis: 100g Fiber

	Zero Kappa			60 Kappa		
	PVAc	No PVAc	Difference	PVAc	No PVAc	Difference
IN						
Fiber	100	100	0	100	100	0
PVAc	6.1	0	6.1	5.8	0	5.8
Total	106.1	100	6.1	105.8	100	5.8
OUT						
Handsheets	88.2	87.4	0.8	92.9	94.5	-1.6
Heavys	8.9	8.7	0.2	2.5	2.8	-0.3
Lights	9.1	3.9	5.2	10.8	3.6	7.2
Total	106.2	100	6.2	106.2	100.9	5.3
Stickie Rating	3	0		4	0	

the PVAc contaminant went. According to Table 2, it all went out as lights in the white water. Note that for the zero kappa pulp 6.1 gm of PVAc contaminant was added to the fiber furnish. The lights collected for this contaminated furnish weighed 9.1 gm. In the series where no PVAc was added, the lights weighed 3.9 gm. The difference is 5.2 gm which can only be explained by the amount of PVAc added to the contaminated series of handsheets. In the 60 kappa pulp, the increase in white water solids due to PVAc contamination is 7.2 gm vs. 5.8 gm added to the system. The negative variance could be due to the inherent variation of the experimentation or it could be due to some fiber fines sticking to the PVAc as it goes through the system.

In summary, 57% of the lights collected could be attributed to the PVAc contaminant for the zero Kappa experiments and 67% for the 60 Kappa experiments. If heavies are included, 29% of total fines can be attributed to PVAc for the zero Kappa experiments and 54% for the 60 Kappa experiments. There are considerably more heavies formed from the zero Kappa experiments than from the 60 Kappa experiments. This is probably because the never dried unbleached pulp forms a better filter mat when the handsheet is formed. In either case, most of the heavies occur during the first two or three handsheets, similar to a start up condition on a paper machine.

Figure 4 is a sheet-by-sheet comparison of basis weights for each series. For all the series, there is a steady increase in basis weight for the first two or three sheets as white water is recycled. After the fourth or fifth handsheet, the increase appears to level out. By the sixth handsheet fiber yield based on basis weight is close to 100%, indicating very little buildup of additional fines in the white water.

Figures 5 and 6 plot white water solids for each handsheet cycle. If PVAc is not added to the system, solids reach a constant level of approximately 0.03% after the third handsheet. If PVAc is added, the white water solids continually increase with each handsheet. After six handsheets, the white water solids are approximately 0.8% and still rising. If all the PVAc continues to pass through the handsheets, it is calculated that the buildup will continue until the white water solids reaches 0.4-0.5% after 35-40 handsheets are made. At this point steady state will be reached.

Although the data of Table 3 suggest very little of the contaminant is retained with the handsheets and very little with the heavies, there has to be some in the handsheets as evidenced by the stickiness rating of the handsheets. This is based on the difficulty of removing the blotters from the handsheets after

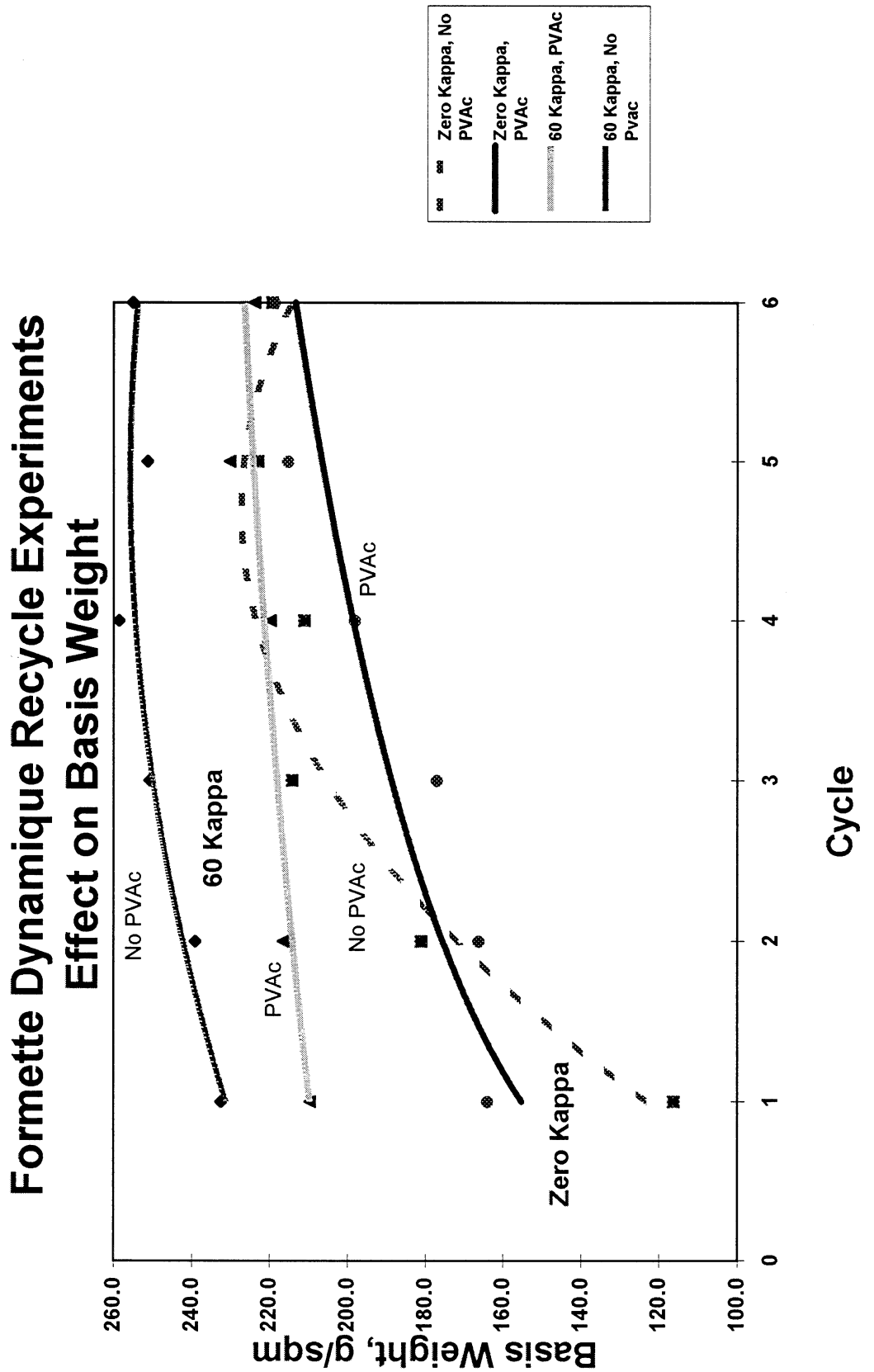


Figure 4
Formette Dynamique Recycle Experiments
Effect on Basis Weight
Basis Weight, g/sqm
Cycle
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
0
1
2
3
4
5
6
No PVAc
60 Kappa
PVAc
No PVAc
PVAc
Zero Kappa
Zero Kappa, No PVAc
Zero Kappa, PVAc
60 Kappa, PVAc
60 Kappa, No Pvac

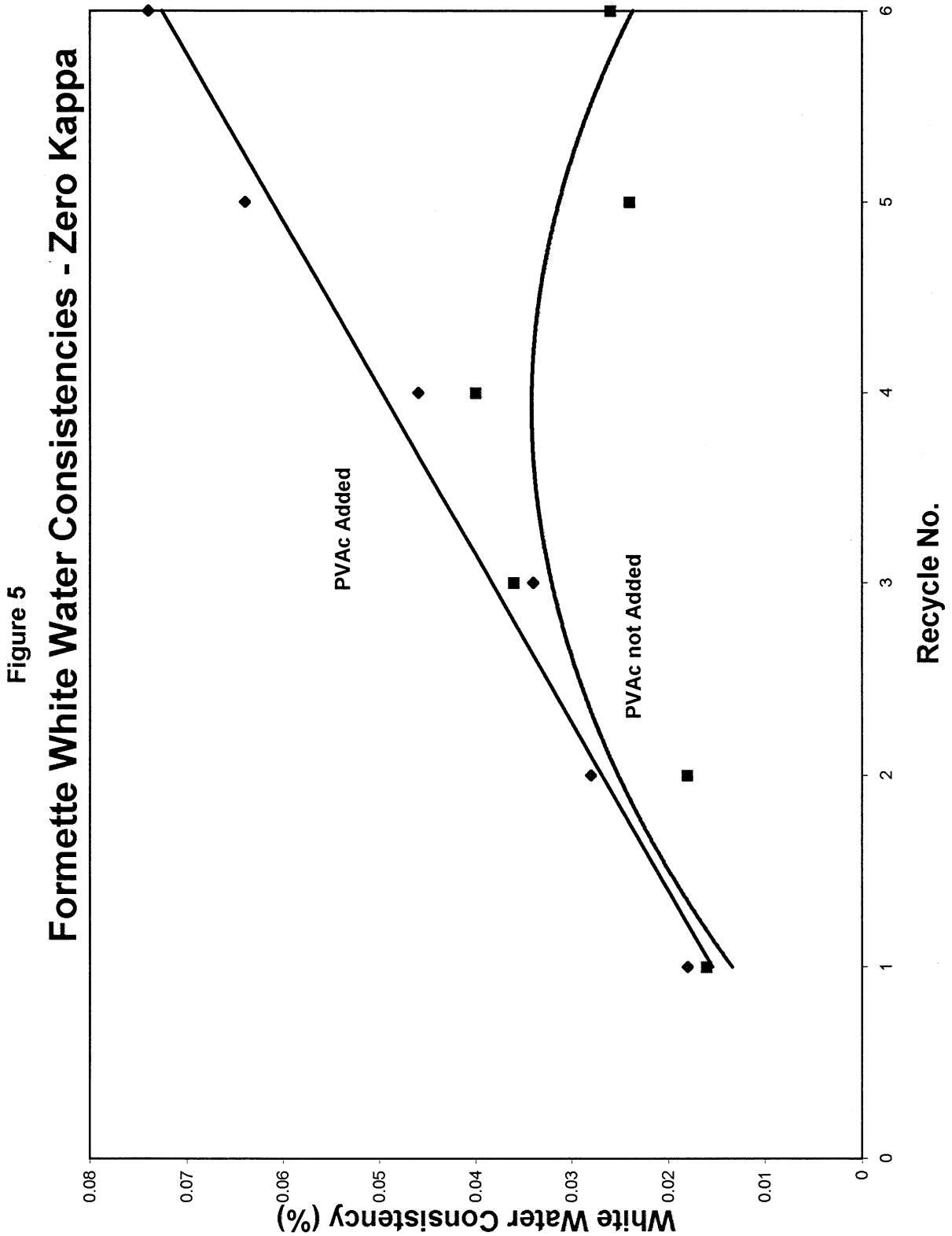
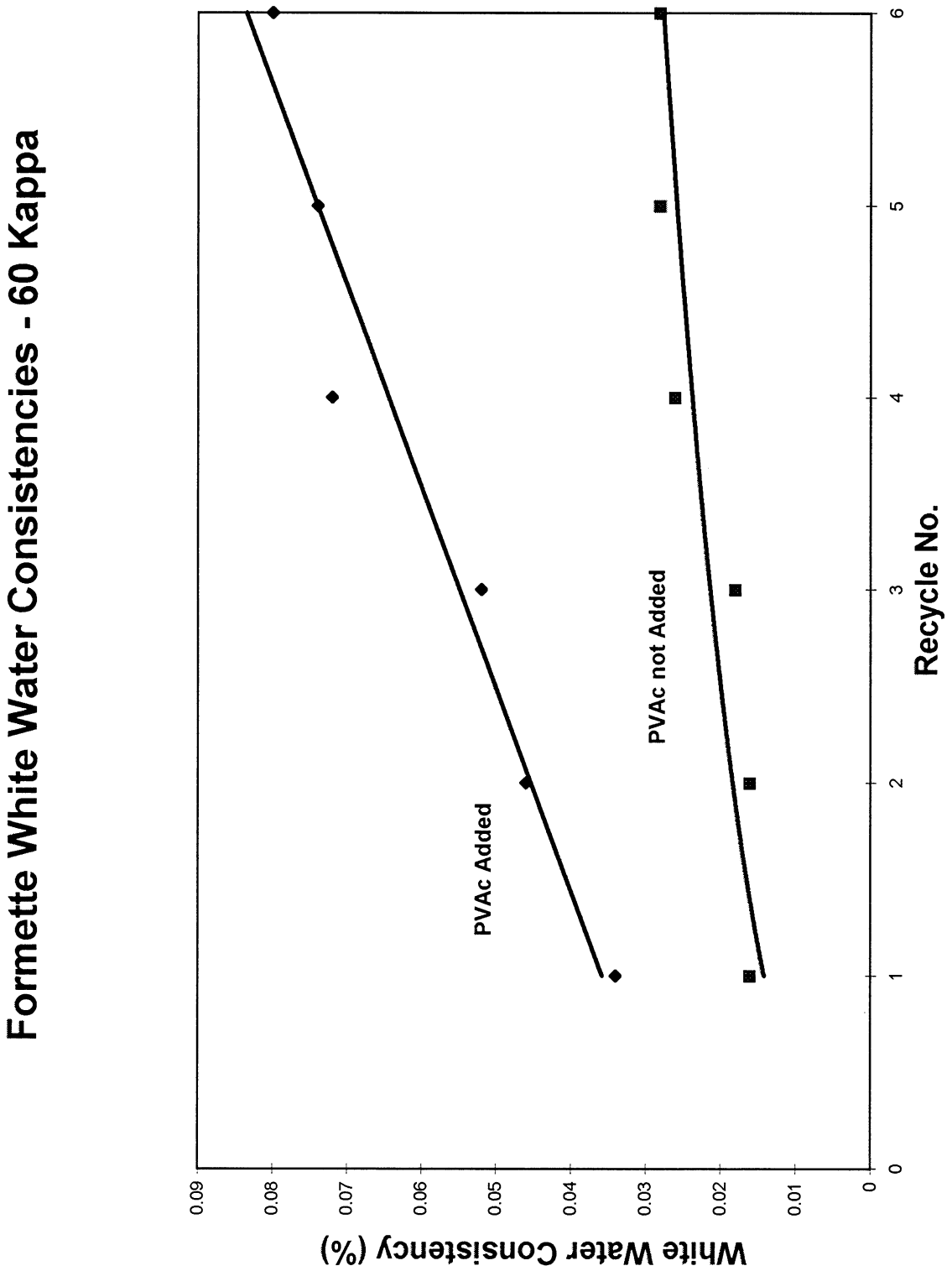

Formette White Water Consistencies - Zero Kappa
White Water Consistency (%)
Recycle No.
PVAc Added
PVAc not Added
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
2
3
4
5
6

Figure 5

Figure 6


Formette White Water Consistencies - 60 Kappa
White Water Consistency (%)
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
1
2
3
4
5
6
Recycle No.
PVAc Added
PVAc not Added

drying. The rating is based on a scale of 1 to 5; 1 being the easiest to remove, 5 being the most difficult. The ratings indicate that the blotters were much more difficult to remove from the handsheets made from pulp containing PVAc contaminant.

Conclusions from the Formette Dynamique Measurements

The principal conclusions from the Formette measurements are as follows.

1. Most of the stickie passed right through the handsheet and ended up as 'lights" in the white water.
2. The stickie material had to be very small in particle size since it could not be filtered by the sheet forming process of the Formette.
3. Since the stickie particles ended up as "lights" in the white water, they had to be either lower in density than water, colloidal in their particle size, or both.
4. The stickie material continually build up in the white water in accordance with the amount that was recycled plus the amount of fresh stickie added with each handsheet.
5. If the stickie particles are small enough to be colloidal in nature, they would be very difficult to separate from the water in a white water recirculation system. They would be too small to filter by a disc filter or saveall. They would not separate in a centrifugal cleaner, and if small enough, they would not separate by a reverse cleaner.
6. Although most of the stickie passed right through the handsheets, enough was retained to make the handsheets "sticky".

With reference to item 1, Steve White (Weyerhaeuser) in a private communication has advised that it is possible for water to overflow around the sides of the Formette handsheet as it is being formed

and carry the fines with it. If this has happened, then some of the fines may have bypassed the handsheet instead of passing through it. This could possibly alter some of the conclusions presented here. The experimentation will be checked

Synopsis of the 1990-1994 Stickies Literature

The literature on stickies was reviewed between 1990-1994 principally through citations from the IPST PAPERCHEM database. A synopsis is as follows.

Typical stickies reported in the literature are: PSA: isoprene polymer, acrylates; Hot melts: PVA, EVA, phthalate esters, polyethylene; Wax. Typical cures suggested include

- Solvent cleaning (drawbacks: solvent increases tack of stickies when released into the system; environmental problems)
- Detackification with talc, zirconium, and various polymers. Synthetic polypropylene fibers have also been used.
- Dispersion to break down particle size and prevent reagglomeration It is commonly believed that small stickies are acceptable if they do not reagglomerate. Large stickies are also acceptable (prior to screening and cleaning) since they can be screened out. Intermediate stickies cause problems.

Conclusions from the Literature Survey

1. PVAc agglomerates in water, but not in the presence of fiber.
2. Retention aids increase K_d dramatically.

3. **K_d is linear with kappa no. Surfactant only has an effect at high kappa.**

4. **Once attached to fiber, PVAc is not easily removed.**

5. **K_d is affected by pH.**

IMPROVED PERFORMANCE OF RECYCLED FINES

STATUS REPORT

FOR

PROJECT F009-01

John F. Waterhouse
Ye Xiao-Liang

March 22 - 23, 1995

Institute of Paper Science and Technology
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Atlanta, Georgia

PROJECT SUMMARY FORM
UTILIZATION OF RECYCLED FIBERS

Project Title:	Improved Performance of Recycled Fines
Project Code:	RECYC
Project Number:	3681-6/FOO9-01
Division:	Engineering and Paper Materials
Project Staff:	John F. Waterhouse, Ye Xiao-Liang
Budget (FY93-94)	$93,980
Reporting Period:	FY94-95

OBJECTIVE

Determine the optimum treatment of the long fiber and fines fractions of a recycled furnish in order to maximize recycled fiber utilization and minimize energy consumption.

SUMMARY

1. The influence of never dried and once dried unbleached kraft fines on drainage behavior and strength-related properties has been investigated.

2. The fines content and performance of selected commercial linerboard and medium samples have been measured together with an assessment of their fines performance.

4. The mechanical treatment of medium and liner fines employing both ultrasonic and small particle impact "refining" methods has been investigated.

5. A paper titled "Improving the Fines Performance of Recycled Pulps," has been prepared for presentation at the upcoming TAPPI Recycling Meeting, New Orleans, February 1995.

GOALS

1. Determine the mechanism(s) responsible for the impaired performance of different sources of recycled fines.

2. Determine if chemimechanical treatments can restore or enhance the papermaking performance of recycled fines.

3. Seek external funding to complement the Institute's member company recycling program.

INTRODUCTION

The papermaking potential of a pulp can be lost through drying, contamination, aging, and fiber damage. All of these factors need to be considered when examining the performance potential of recycled fibers.

Recycled fibers, particularly those from chemical pulps, make sheets that are generally weaker and slower draining than those from virgin pulps. To overcome this problem, it is not unusual in manufacturing to discard the fines material and restore the strength of the sheet by refining the long fiber fraction. This procedure is successful, but can be costly in terms of refining energy, pulp yield, and landfill requirements.

It is generally agreed that fines contribute appreciably to the strength of virgin pulp sheets (1), especially for pulps of thick-walled species such as Southern pine and for mill-refined pulps. However, after drying their contribution to strength-related properties is usually negligible and can adversely affect drainage. Although it is known that recycled fines contribute little to strength, precise reasons for their ineffectiveness are unknown. Virgin and recycled pulps are composed of long fiber and fines fractions. We use the generally accepted definition of fines as the pulp fraction which passes through a 200 mesh screen.

VIRGIN VERSUS RECYCLED FURNISHES

FURNISH = LONG FIBER FRACTION + **FINES FRACTION (>200 MESH)**

Issues:

* Hornification and Other Degrading Effects
* Stickies and Contamination
* Deinking
* Solid Waste Reduction
* Energy

Fines material can be further categorized depending on pulp type, i.e., mechanical, chemical, virgin, or recycled. The properties of fines will also depend on where they originate. We will use the definitions given in Table 1 in our discussion of fines.

TABLE 1. FINES NOMENCLATURE.

CYCLE	PRIMARY	"PRIMARY"	"SECONDARY"	SECONDARY
		"Unrefined"		Refined
VIRGIN FINES F_0	P_0	-	-	S_0
ONCE DRIED F_1	-	P_{0d1}	S_{0d1}	S_1
TWICE DRIED F_2	-	P_{0d2}	$S_{0d2} + S_{1d1}$	S_2
THRICE DRIED F_3	-	P_{0d3}	$S_{0d3} + S_{1d2} + S_{2d1}$	S_3

As an example, the fines present in twice dried refined pulp F_2 consist of:

$$F_2 = P_{0d2} + S_{0d2} + S_{1d1} + S_2$$

The primary fines P_0 present in a virgin pulp prior to refining consist mainly of ray and parenchyma cells, and represent around 1% to 8% of the furnish. They are regarded as filler material and do not contribute significantly to paper properties (2). On the other hand, secondary fines S_0 do contribute positively to many paper properties, although they do have an adverse effect on drainage and water removal (2) (3).

The fines present in a once dried pulp consist of a portion of dried primary fines P_{0d1}, and dried secondary fines S_{0d1}. These fines, which are the main subject of our proposal, tend to perform like primary P fines, i.e., as a filler material. On the other hand, the secondary fines S_1, produced by refining a once dried pulp, tend to equal or better the performance of virgin secondary fines S_0 (3) (4).

It is also important to know what the likely level of recycling is within a furnish, and this will obviously depend on the level of recycled fiber utilization one wants to achieve. This question has been addressed by Howarth and Rogers (5) and by Cardwell and Alexander (6) whose equation is given below.

$$EPn = (100 - P)(P/100)^n \qquad (1)$$

where EPn is the equilibrium percentage of fiber recycled n times, and P is the target percentage of fiber to be utilized. Using equation (1), the percentage of the total furnish which has been recycled 1, 2, 3, 4, and 5 times for different utilization rates is given in Table 2.

TABLE 2. PERCENTAGES OF FURNISH WHICH HAS BEEN RECYCLED FOR 1, 2, 3, 4, AND 5 TIMES FOR DIFFERENT UTILIZATION RATES.

Number of Recycles	% RECYCLED FIBER UTILIZATION					
	20	**40**	**50**	**60**	**70**	**80**
0 (virgin)	80	60	50	40	30	20
1	16.0	24.0	25.0	24.0	21.0	16.0
2	3.2	9.6	12.5	14.4	14.7	12.8
3	0.64	3.84	6.25	8.64	10.3	10.2
4	0.13	1.54	3.13	5.18	7.20	8.19
5	0.03	0.61	1.56	3.11	5.04	6.55
TOTAL %	99.87	99.59	98.44	95.33	88.23	73.74

Achieving a target of 50% recycled fiber utilization by the year 2000 (7) means that approximately 25% of the total furnish will have been recycled on average more than once.

We assume that fractionation of a recycled pulp will enable a more appropriate treatment of the long fiber and fines fractions. Treatment of the long fiber fraction will probably involve some level of refining and possibly chemical treatment to reverse the effects of drying and remove defects, while minimizing fiber damage and fines production. This strategy has been suggested by Musselmann (8) as a way to reduced energy consumption.

In many instances, recycling does involve fractionation, but the fines fraction ($P_{0d1} + S_{0d1}$) of the pulp is disposed of, and a portion of the long fiber fraction is also lost. When deinking is

involved, in addition to fines, filler, ink particles, and other contaminants are also disposed of as solid waste. **However, our main goal is to recover the papermaking potential of the fines fraction $S_{0d1} + S_{0d2} + ...$** in order to make fractionation a more effective process and reduce material currently going to landfill.

One of the main factors contributing to the loss in papermaking potential of a recycled pulp is drying. The effect is known as hornification and results in a loss of swelling of both the long fiber and fines fractions (9) after they have been dried and rewet. Scallan and Laivins (10) have recently shown, using infrared analysis and deuterium exchange, that hornification of a fines free pulp is the result of irreversible hydrogen bond cross links formed between microfibrils during drying, i.e., these bonds are not broken upon rewetting.

Scallan and Tigerstrom (11) in earlier work demonstrated, using predictions of transverse fiber modulus, that hornification of the long fiber fraction can be reversed by refining. They also found no evidence of hornification in pulps above a yield of about 70%. Gavelin, Kolmodin, and Treiber (12) found, using critical point drying (cpd), that "hornification" (collapse of structure due to surface tension forces) of mechanical fines could be readily reversed upon rewetting. No similar study has been made of chemical pulp fines.

The mechanism proposed by Scallan and Laivins (10) for hornification of the long fiber fraction might also be presumed to hold for the fines fraction when the pulp yield is less than 70%.

Mancebo and Krokoska (2) found that refining does not reverse fines hornification even though refining does reverse fiber hornification (7). No reasons were given for why this was so, yet this difference is crucial for understanding the ineffectiveness of the fines. This finding might be an indication that other factors in addition to hornification, e.g., agglomeration, changes in wetting behavior, and ineffective communication of mechanical stresses to the fines fraction might be involved.

Therefore, a necessary step in our research program is to determine why the papermaking performance of fines is adversely affected by drying and why refining does not restore it. This knowledge will enable us to design specific chemimechanical treatments to either prevent or reverse the adverse effects that drying has on fines. It is anticipated that mechanical action to impart stresses to the fines will be a necessary part of the treatment, for example, to reduce agglomeration and reswell the fines. Solute exclusion (13), water retention values (9), and drainage resistance measurements (4) have shown that there is a much higher association of water with the fines than the long fiber fraction. Owing to the smaller dimensions of the fines and surface tension effects, caution has to be exercised when interpreting the extent of fines-water interaction.

It is interesting to note that fines S_1, produced by refining a once dried pulp, are comparable in performance to virgin secondary fines S_0 (3) (4). This implies that drying does not alter the cellulose-water interaction of new surfaces created by refining. However, if changes in crystallinity due to drying occur, as found by Marton et al. (14), this finding may be modified.

There are no theories which satisfactorily account for the contribution of fines in a network. In broad terms, we can say that fines contribute positively to the mechanical properties of paper by reducing stress concentration, effectively increasing interfiber bonding (15), and improving stress transfer. According to Page (16), many effects are associated with the refining of a pulp, and fines production is one of them. However, we are now considering the treatment of fines which have been dried. For the moment, we will assume that the promotion of internal and external fibrillation will be necessary to reswell the fines.

"How effective is fractionation and treatment of the long fiber and fines fractions when compared with treatment of the whole pulp?" is a question which ultimately needs to be answered. Furthermore, on what basis should this judgement be made? Clearly, the first question cannot be answered until promising treatment strategies have been devised. Treatment of the long fiber fraction should not be problematical; however, effective treatment of the fines fraction is expected to be quite challenging.

We have already stated that we expect an effective fines treatment to involve both chemical and mechanical approaches as indicated in Figure 1. In the next section, we present some results on the mechanical treatment of fines.

Papermaking is essentially a balance between water removal and property development. Water removal occurs by several mechanisms including drainage in the forming section, removal by couching and wet pressing, and finally drying. These processes also control final sheet properties through consolidation and shrinkage control.

As yet, we do not have an agreed laboratory method or approach to evaluating the "real world" papermaking potential of a furnish, i.e., the relative balance between water removal and property development of pulps relevant to paper machine operation. In classical pulp evaluation studies, all steps of the papermaking process are held constant, i.e., forming, couching, wet pressing, and drying, and only refining is varied. Water removal and property development are judged in terms of a drainage measurement, i.e., Canadian Standard Freeness, and paper properties, i.e., tensile, tear, etc. Despite the criticism of freeness and drainage measurements, this approach is well recognized and at least provides a first, albeit crude, indication of how a pulp will perform.

More sophisticated methods exist for characterizing the water removal behavior of a pulp, e.g., hydrodynamic pulp characterization, solute exclusion technique (water retention value), and for relating strength properties to fiber and network properties, e.g., the tensile strength equation of Page (16). However, these approaches are not routinely employed, nor are they, as yet, interrelated.

Cardwell and Alexander (6) have expressed the water removal-strength property relationship for recycling by how the number of recycles affects the strength-freeness envelope which is shown in Figure 2. For a target strength level, the bad news is that a reduction in freeness seems to be inevitable when compared with the virgin fiber. Ways to circumvent this which have been previously discussed include refining a fines-free recycled furnish, fractionation and separate treatment of the long fiber and fines fraction, additives, chemical treatment, or increasing basis weight.

Machine speed sensitivity and, hence, productivity to drainage have been emphasized by de Ruvo and Htun (18). Their relationship for a furnish containing 25% recycled furnish is shown in Figure 3.

RESULTS AND DISCUSSION

Goal 1. Determine the mechanism(s) responsible for the impaired performance of different sources of recycled fines.

We have speculated that the loss in fines performance due to recycling may be due to hornification, agglomeration, curl, contaminants, loss of hemicelluloses, and loss of adhesion.

In our work to date, we have relied almost exclusively on Canadian Standard Freeness (CSF) measurements to infer what changes in hydrodynamic surface area may have occurred during recycling. Drainage measurements are generally very sensitive to changes in hydrodynamic specific surface area. It is recognized that these losses may result from several of the above factors, and in future work, we will try to delineate them.

The variation of CSF with PFI revolutions for a never dried unbleached southern pine kraft pulp is shown in Figure 4 (open squares). This curve has some interesting features which are reproducible. We note an initial plateau before a rapid drop in freeness occurs followed by a reduced rate of falloff. The initial plateau is believed to be due to the influence of primary fines P_o, while the rapid falloff is due to the production of secondary fines S_o. The reduce rate of falloff in the range of 5000 to 10,000 revolutions is believed to be due to an increase in fines loss through the screen. The variation of freeness for the fines-free pulp is also shown (plus sign). The reduction in freeness is now much lower and is mainly attributed to external fibrillation.

Also shown in Figure 4 are refining results for the long fiber fraction of recycled pulps. These pulps were produced by fractionating (< 200 mesh) reslushed handsheets which were made from pulps refined to 2000 and 4000 revolutions, respectively. Since these pulps contained no primary fines, there is an immediate rapid decrease in freeness. Freeness curves for the refined long fiber fraction pulps with fines removed are also shown in Figure 4. We again note a large loss in hydrodynamic specific surface area due to fines removal, i.e., high CSF values.

The variation of freeness with fines content is shown in Figure 5. The initial plateau occurs over the fines range of 3.7% which is the primary fines content P_o measured on the pulp. In the absence of primary fines, the freeness variation is approximately linear and independent of refining level for the refined long fiber fraction. The recycled or once dried fines obtained by fractionating the reslushed handsheets (> 200 mesh) included 3.7% primary fines. These were added back to the unbeaten pulp, and again, the freeness variation is independent of the initial refining level from which the fines were produced. The extended plateau in this case is due to the primary fines present in the unrefined pulp. Consistent with the results shown in the Figure 4, we conclude that recycling has resulted in an effective loss of surface area of the recycled fines.

Figure 6 compares the impact on freeness of never dried S_o and once dried fines S_{od1} produced at two levels of refining added, as before, to the unrefined never dried pulp. As noted above, the reduction in freeness for the recycled fines is independent of the refining level from which the fines were obtained. In contrast, the never dried fines do appear to be dependent on the refining level at which they were produced.

The variation of apparent density with fines content is shown in Figure 7. Secondary fines are generally fibrous in nature, but have a smaller effective width or diameter than the fibers from which they were removed and thus a high surface area. It is noted that the ability of fines to densify through Campbell's forces and bonding is impaired by recycling. Although more work is required to delineate this effect, it is consistent with a loss in hydrodynamic specific surface area.

The variations of both in-plane and out-of-plane elastic constants with apparent density are shown in Figures 8 and 9. These measurements were made on CSF pads using a previously described procedure (19). Both the once dried and never dried data appear to fall onto a common curve, although there is more scatter in the out-of-plane modulus, especially above a density of 0.85 gm/cm^3. In previous work, we have seen a falloff in modulus for densities higher than about 0.85 gm/cm^3. From Figures 8 and 9 we can infer that in order to achieve a given level of elastic properties at fixed fines content, the recycled fines will need to be treated in such a way as to restore their ability to consolidate the web through Campbell's forces.

Recycling of Linerboard and Medium

In previous work (19), we have examined the effect of various chemical treatments on OCC. To gain further insight into OCC, we have also examined the recycling behavior of its major components, i.e., linerboard and medium.

The properties of medium and liner samples taken from IPST's inventory are given in Tables

3 and 4. We see that the average fines content range of the mediums and liners is 12.6% and 6.4%, respectively. Properties of the 100% Kraft liner and 100% NSSC virgin medium prior to repulping are given in Table 4 (denoted by an asterisk in Table 3). The levels of compressive strength for the repulped samples are remarkably high. In previous work (20), we have found that for high density sheets made on the Formette Dynamique, STFI compressive strength approaches a value of around 30 Nm/g. In both cases, we had z-direction restraint to minimize sheet shrinkage during drying. We also note the large differences in out-of-plane longitudinal modulus when comparing the reslushed samples and the original board materials. This is partly due to the higher density of the remade pads, and possibly the adverse effects of calendering on the commercial boards.

Losses in liner properties due to recycling are not expected to be large since only minimum refining is used, and the fines production is not large, especially when one considers that the fines content includes some level of primary fines. Losses in medium properties due to recycling may be higher depending on the yield (we will obtain yield measurements for these samples).

In our previous work (19) with caustic treatment of OCC, the untreated compressive strength level was 29.5 Nm/g at a fines level of 15% (fines range of OCC is 12 to 25% depending on its source). This value is close to those shown in Table 3. At this fines level, a 2% caustic treatment improved compressive strength by about 14%.

Larger quantities of liner and medium fines from the commercial boards denoted by an asterisk

in Table 3 were produced by fractionation using a Sweco screen. The influence of these fines on CSF is shown in Figure 10. We infer that liner fines have a greater hydrodynamic specific surface area at given fines content than the medium fines. This difference may reflect a yield difference alluded to previously. Also shown in Figure 10 is the behavior of the once dried unbleached kraft pulp fines produced at two levels of refining which we discussed earlier.

The impact of liner and medium fines added to an unbeaten never dried kraft pulp on properties is given in Table 5. There are no significant changes in pad densification as a result of either medium or liner fines addition. The in-plane elastic constant with medium fines addition is unaltered, while the out-of-plane constant shows a slight decrease. Liner fines addition produces a 16.5% increase in in-plane elastic constant.

Also included in Table 5 for comparison is the addition of never dried unbleached and bleached kraft fines obtained from a bleached kraft pulp beaten to 100 ml CSF. We now see over the same fines range a large increase in sheet density, and a concomitant increase in in-plane elastic constant of 21%. Interestingly, the out-of-plane elastic constant increases initially and then decreases.

We have not completed all of our measurements and analysis of the liner and medium fines. We thought that the bleached kraft fines might be representative of what we could expect if the medium and liner fines were subjected to a mild kraft cook. We have see an improvement in properties using never dried bleached kraft fines. Whether the poorer performance of the medium and liner fines is due to yield, contamination, etc., remains to be determined. In the

introduction, we stated that Scallan and Laivins (10) had found that hornification does not occur above a yield of 70%, at least for the long fiber fraction. However, it is hypothesized that high yield fines, even in the absence of hornification, will not be as effective as low yield fines.

In what follows, we have performed some exploratory experiments to determine if mechanical treatment of fines is effective.

TABLE 3. FREENESS, FINES CONTENT, AND PROPERTIES OF REPULPED MEDIUM AND LINER SAMPLES (CANADIAN STANDARD FREENESS PADS BASIS WEIGHT 370 g/m^2)

TYPE	FURNISH	CSF ml	FINES %	APPARENT DENSITY g/cm^3	IN-PLANE MODULUS (k/sec)^2	OUT-OF-PLANE MODULUS (k/sec)^2	STFI COMPRESSIVE STRENGTH Nm/g
Medium	20% recycled green liquor	556	13.2	0.873	10.7	0.575	38.3
Medium *	semichem. virgin	513	12.0	0.834	10.3	0.427	31.7
liner *	100% Kraft virgin	688	4.5	0.849	9.68	0.430	30.2
liner	40% virgin 60% OCC	669	8.2	0.806	10.9	0.354	36.2
liner		628	4.8	0.893	8.89	0.424	30.7
liner	100% kraft virgin	685	5.53	0.871	9.79	0.340	29.0
liner	40% virgin 60% OCC	617	8.8	0.826	10.8	0.364	29.7

TABLE 4. PROPERTIES OF ORIGINAL MEDIUM AND LINER SAMPLES. (FROM IPST INVENTORY)

TYPE	FURNISH	BASIS WEIGHT g/m^2	APPARENT DENSITY g/cm^3	MEAN IN-PLANE MODULUS $(k/sec)^2$	OUT-OF-PLANE MODULUS $(k/sec)^2$	MEAN STFI COMPRESSIVE STRENGTH Nm/g
Liner *	100% Kraft Virgin	168.6	0.786	10.7	0.575	29.2
Medium *	semichem. virgin	120.6	0.624	6.08	0.143	22.9

TABLE 5. PROPERTIES FOR MEDIUM AND LINER FINES ADDITION TO AN UNBEATEN NEVER DRIED KRAFT PULP.

FINES %	0	7.5	15	30
MEDIUM FINES				
CSF ml	750	689	698	649
APPARENT DENSITY g/m^2	0.811	0.788	0.792	0.805
IN-PLANE ELASTIC CONST. (k/sec)^2	10.3	11.3	10.7	10.7
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.471	0.397	0.449	0.433
LINER FINES				
CSF ml	750	613	624	414
APPARENT DENSITY g/m^2	0.811	0.828	0.817	0.787
IN-PLANE ELASTIC CONST. (k/sec)^2	10.3	11.4	11.6	12.0
0UT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.471	0.434	0.512	0.452
NEVER DRIED UNBL. KRAFT FINES				
CSF ml (2000R) (4000R)	750	750 698	593 512	301 244
APPARENT DENSITY g/m^2 (2000R) (4000R)	0.811	0.803? 0.847	0.935 0.863	0.952 0.962
IN-PLANE ELASTIC CONST. (k/sec)^2 (2000R) (4000R)	10.3	10.2? 11.2	11.6 12.3	12.8 12.7
0UT-OF-PLANE ELASTIC CONST. (k/sec)^2 (2000R) (4000R)	0.471	0.495 0.547	0.528 0.586	0.534 0.636
NEVER DRIED BL. KRAFT FINES				
CSF ml	750	666	600	241
APPARENT DENSITY g/m^2	0.835	0.883	0.911	1.04
IN-PLANE ELASTIC CONST. (k/sec)^2	10.4	11.2	11.9	12.6
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.485	0.633	0.515	0.479

Goal 2. Determine if chemimechanical treatments can restore or enhance the papermaking performance of recycled fines.

In earlier work, we have briefly examined different chemical treatments including sodium hydroxide, peroxide, and ozone. We now turn our attention to the mechanical treatment of fines. We assume that some form of "refining" action is necessary to reswell or internally fibrillate the fines. This precept may be modified as we learn more about why recycling has such an adverse effect on fines performance.

In exploratory work, we have briefly examined ultrasonic treatment and small particle impact "refining" of the fines.

Ultrasonic Treatment of Fines

The ultrasonic treatment of medium and liner fines has been carried out using a horn vibrating at 20 kHz. The fines (20 ml) were treated at various consistencies and times. The variation of temperature with time and consistency is shown in Figure 11. We see that the presence of fines reduces the temperature rise. It is noted that at 5% consistency the temperature rise for the liner fines is greater than the medium fines; this perhaps implies that there is more energy absorbed by the medium fines than the liner fines. In addition to fines treatment, the never dried unbleached kraft pulp control was also refined at 5% consistency for 6 minutes to determine if any refining action was evident.

A summary of the properties for these treatments is given in Table 6.

TABLE 6. PROPERTIES FOR ULTRASONIC TREATED MEDIUM AND LINER FINES AT 15% ADDITION TO AN UNBEATEN NEVER DRIED KRAFT PULP.

TREATMENT TIME MINS.	0	6	10
MEDIUM FINES			
CSF ml	698	683	693
APPARENT DENSITY g/m^2	0.792	0.914	0.881
IN-PLANE ELASTIC CONST. (k/sec)^2	10.7	11.5	11.5
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.449	0.536	0.442
LINER FINES			
CSF ml	624	630	647
APPARENT DENSITY g/m^2	0.817	0.911	0.882
IN-PLANE ELASTIC CONST. (k/sec)^2	11.6	11.9	11.9
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.512	0.449	0.522
TREATMENT OF LONG FIBER FRACTION (never dried unbleached kraft pulp)			
CSF ml	750	730	-
APPARENT DENSITY g/m^2	0.811	0.837	-
IN-PLANE ELASTIC CONST. (k/sec)^2	10.3	11.9	-
0UT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.471	0.475	-

There is some evidence that the ultrasonic probe is effective in producing some refining action. As shown in Table 6, changes in density and out-of-plane elastic constant are small, but there is an increase of 14.4% in in-plane elastic constant. By comparison, the medium fines seem to respond to ultrasonic treatment more than the liner fines. The apparent density, in-plane and out-of-plane elastic constants are increased by 15%, 6.5%, and 19.4%, respectively. This is consistent with the finding that more energy appears to be absorbed by the medium fines as judged by the temperature rise.

Small Particle Impact "Refining" of Fines

We conjecture that producing desirable changes in fiber or fines structure may be better achieved by impacting the fiber or fines with particles which are of the same size as these elements. However, creating this impact situation with acceptable particles is not a simple matter. Cumpston (21) reports that exceptional refining effects were found when fibers were refined with sand. It is known that when fibers are refined in a ball or rod mill fiber damage can be excessive.

Small particle impact "refining" has been explored using sand and small brass balls (0.125" diameter). The impacts have been produced by shaking, both by hand and machine, as well as stirring. Separation of the particles is easier for the large brass balls than for the sand.

Table 7 shows some limited results for the impact "refining" of medium and liner fines using 1/8" diameter corrosion-resistant brass balls. The medium and liner fines (1 gram) were

refined at 12.0% and 8.6% consistency, respectively, using 650 balls. Untreated and treated fines were added at the 15% level of addition to the unrefined never dried unbleached kraft control as used earlier.

It appears that some "refining" action has been achieved with this treatment. It is also evident that treatment for 80 minutes was possibly too severe. Changes in density, in-plane and out-of-plane elastic constants at 30 minutes are 13.2%, 0.9%, and -3.3% for the liner treated fines, and 20.8%, 10.3%, and 8.5% for the medium fines. Again it appears that the medium fines have responded better to treatment than the liner fines.

TABLE 7. PROPERTIES FOR SMALL PARTICLE IMPACT "REFINED" MEDIUM AND LINER FINES AT 15% ADDITION TO AN UNBEATEN NEVER DRIED KRAFT PULP.

TREATMENT TIME MINS.	0	30	80
MEDIUM FINES			
CSF ml	698	677	703
APPARENT DENSITY g/m^2	0.792	0.957	0.895
IN-PLANE ELASTIC CONST. (k/sec)^2	10.7	11.8	10.7
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.449	0.487	0.524
LINER FINES			
CSF ml	624	645	580
APPARENT DENSITY g/m^2	0.817	0.925	0.939
IN-PLANE ELASTIC CONST. (k/sec)^2	11.6	11.8	12.0
OUT-OF-PLANE ELASTIC CONST. (k/sec)^2	0.512	0.495	0.403

TABLE 8. SUMMARY OF CHANGES FOR VARIOUS TREATMENTS AT THE 15% FINES ADDITION LEVEL.

PROPERTY OR % CHANGE	CONTROL fines-free N.D Unbl. K	MEDIUM FINES ADDITION	N.D.BL.K. FINES ADDITION	ULTRASONIC TREATMENT 6 MINS	IMPACT REFINING Brass Balls	2% NaOH Treatment of 15% OCC
CSF	750	698	600	683	677	575
ρ g/cm^3	0.811	0.792	0.911	0.914	0.957	0.775
STFI Nm/g						33.5
$\Delta(\rho)$	-	-2.3	9.1	15	20.8	3
$\Delta(C/\rho)$	-	3.9	14.4	6.5	10.3	10.3
$\Delta(C_{33}/\rho)$	-	-4.7	6.2	19.4	8.5	13.7
Δ(STFI)	-					13.6

CONCLUSIONS AND SUMMARY OF TRENDS

We have investigated the behavior and mechanical treatment of various types of fines. The following is a summary of our findings and tentative conclusions.

1. Changes in CSF are a sensitive indicator of losses in surface area due to recycling (drying).

2. The initial plateau region of the CSF variation with fines content is attributed to the level of primary fines present.

3. The fines play an important roll in sheet consolidation and densification through the Campbell effect. Drying has an adverse affect on the densification potential of fines; however, the in-plane elastic constant-density relationship does not appear to be changed by recycling.

4. There is a significant dropoff in out-of-plane elastic constant for densities greater than about 0.85 g/cm^3. It is not yet known whether this is real or a measurement artifact.

5. Average fines content of some commercial mediums and liners average is 12.6% and 6.4%, respectively. Surprisingly high property values were obtained for repulped commercial samples indicating that recycling may not have adversely affected the compressive strength potential of the reslushed pulp. Nevertheless, commercial medium

and liner fines exhibited the effects of recycling (drying) when their performance was compared with both never dried unbleached and bleached kraft fines.

6. Both ultrasonic (20 kHz) and small particle (1/8"diameter brass balls) impact "refining" have produced significant changes in properties particularly for recycled medium fines.

7. An attempt to compare the various forms of treatment which have been investigated is shown in Table 8 for a 15% addition of medium fines to an unrefined never dried unbleached kraft pulp. A 15% addition of medium fines produces little change in properties; however, small particle impact "refining" significantly improves their performance. A 2% caustic treatment produces a similar improvement.

8. We are encouraged from the results that a suitable chemimechanical treatment might be found to reverse the adverse effect that drying has on fines performance.

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REVERSING THE EFFECTS OF DRYING

* TREATMENT OF LONG FIBER FRACTION

Defects Present - Hornification, Microcompressions, Curl, Contaminants, Loss of Hemicelluloses.

* TREATMENT OF FINES FRACTION

Defects Present - Hornification, Curl, Contaminants, Loss of Hemicelluloses, Agglomeration, Loss of adhesion.

Mechanical Treatment	**Chemical Treatment**
Refining	Sodium Hydroxide
Ultrasonic	Ozone
Homogenizer	Peroxide
Colloid	Enzyme
Small Particle Impact Refining	

RESWELLING MECHANISMS

Mechanical Stress + Osmotic Stress

Figure 1. Reversing the Effects of Drying.

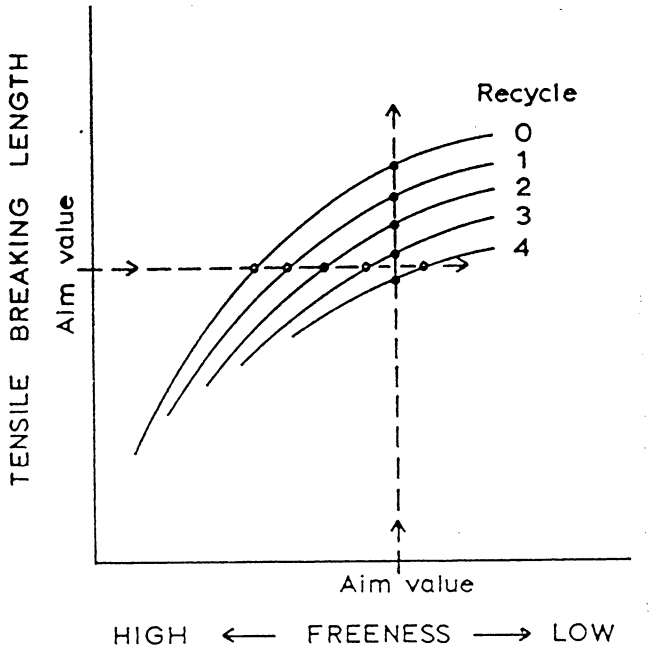

Fig. 5 — Breaking length versus freeness of recycled pulps.

Figure 2. Variation of Tensile Strength with Freeness (CSF) and Effects of Recycling (Taken from Cardwell and Alexander (6)).

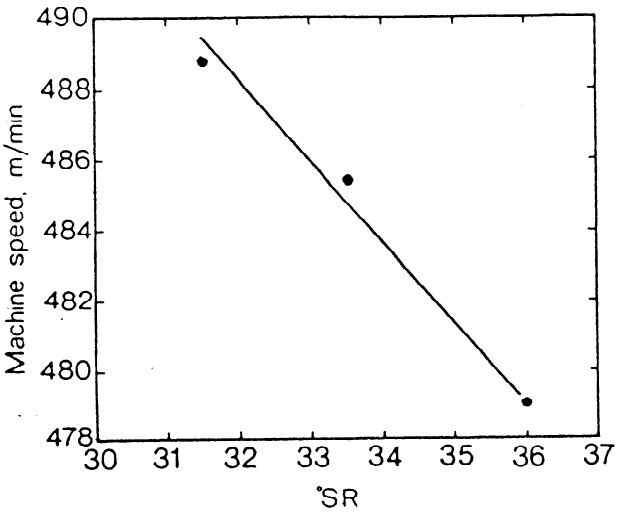

Figure 3. Variation of Machine Speed with Drainage Resistance (°SR) (Taken from de Ruvo and Htun (18)).

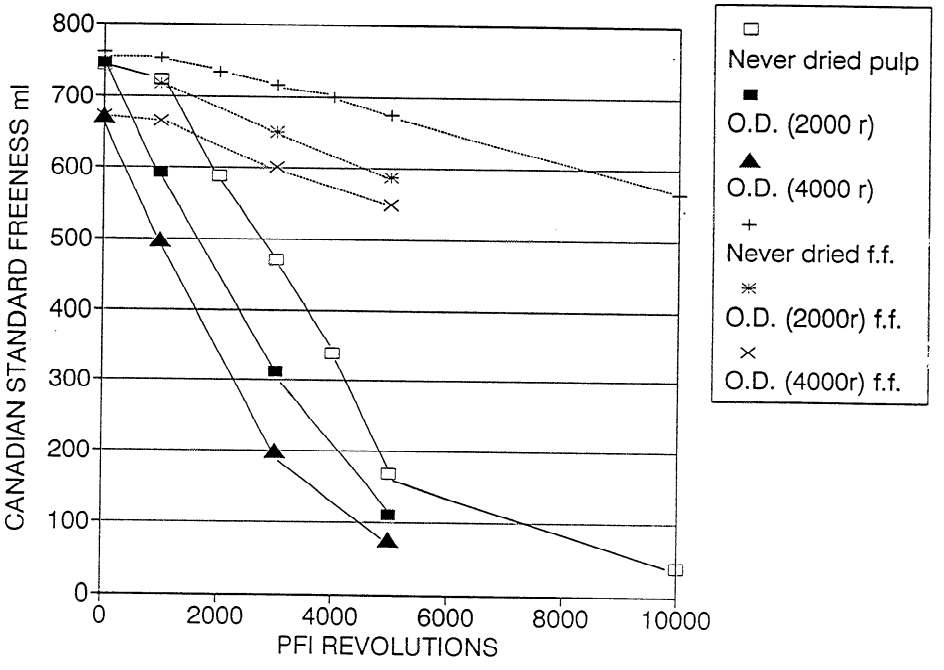

Figure 4. Variation of Canadian Standard Freeness with PFI Revolutions for Refining of Never Dried and Once Dried Fines-free Unbleached Kraft Pulp and Effects of Fines Removal.

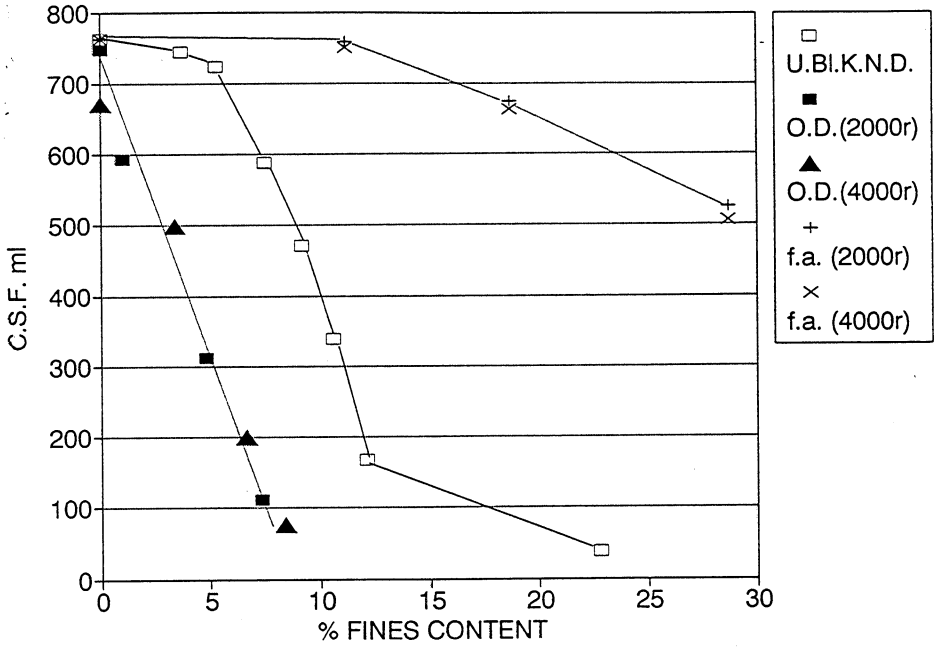

Figure 5. Variation of Canadian Standard Freeness with Fines Content for Refined Never Dried and Fines-free Once Dried Unbleached Kraft Pulps, and for Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

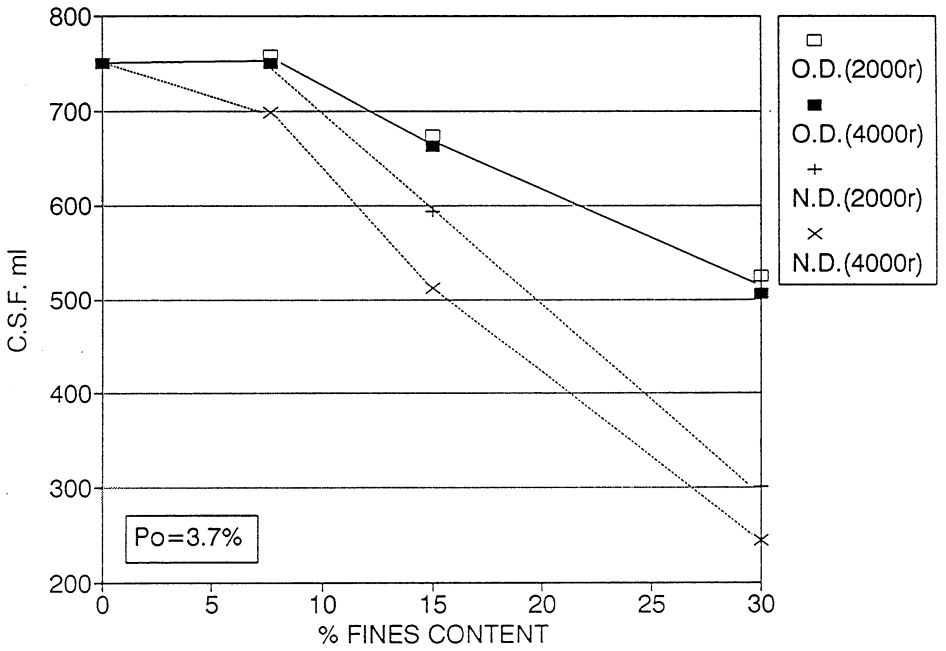

Figure 6. Variation of Canadian Standard Freeness with Fines Content for Never Dried and Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

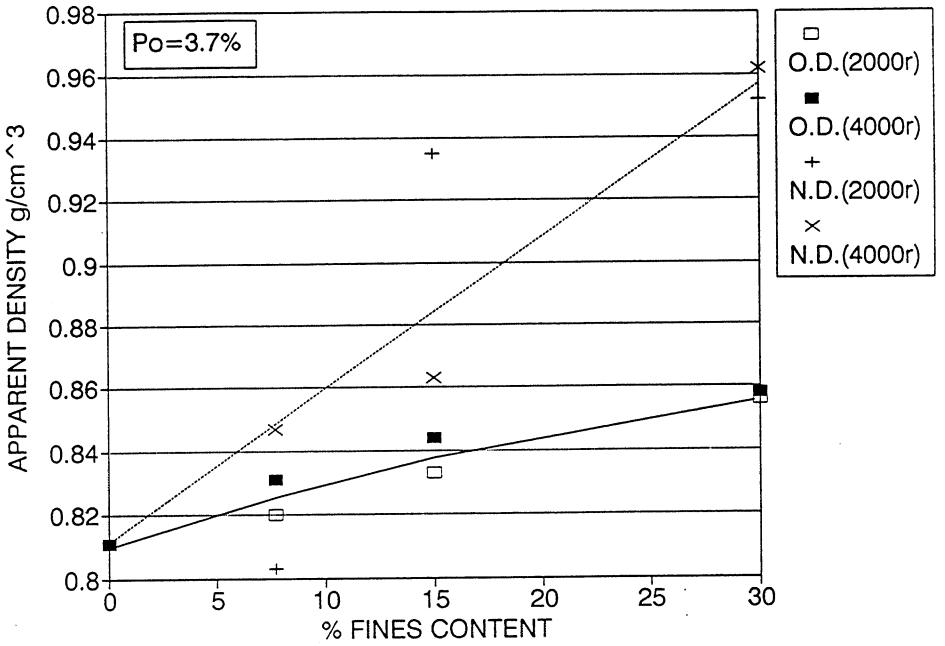

Figure 7. Variation of Apparent Density with Fines Content for Never Dried and Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

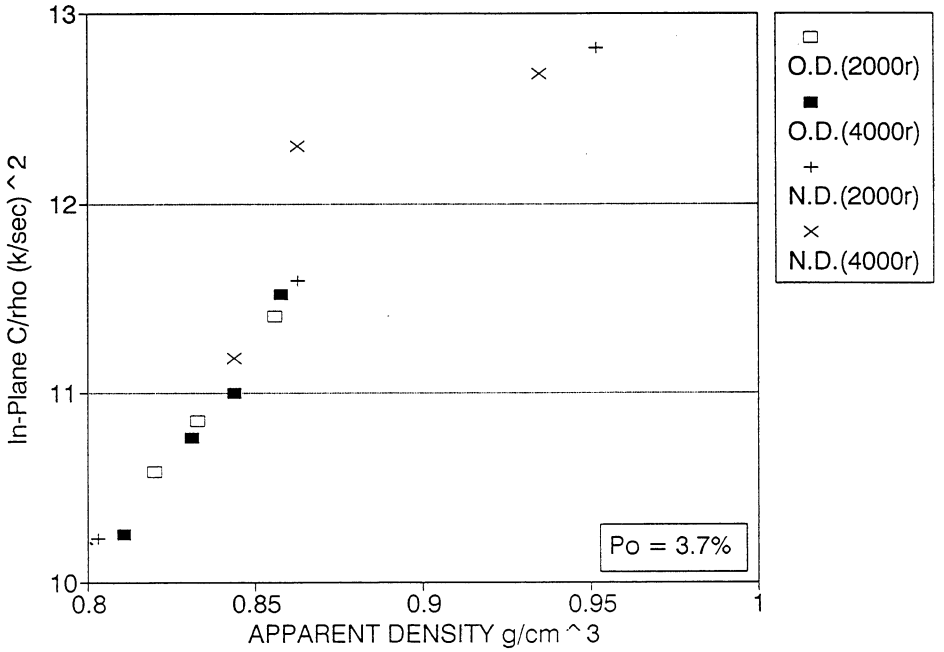

Figure 8. Variation of In-Plane Elastic Constant with Fines Content for Never Dried and Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

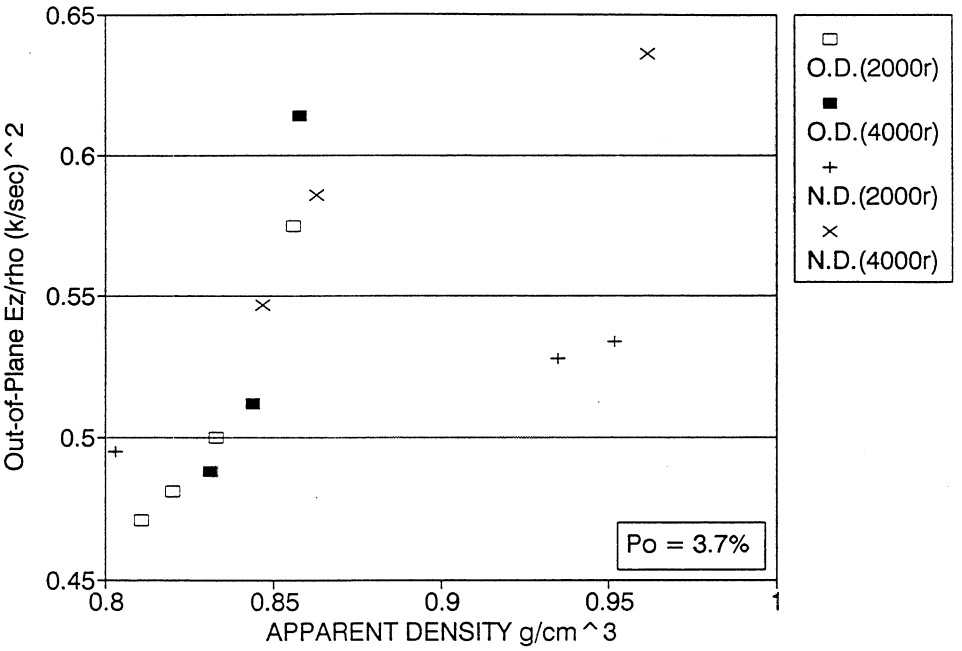

Figure 9. Variation of Out-of-Plane Elastic Constant with Fines Content for Never Dried and Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

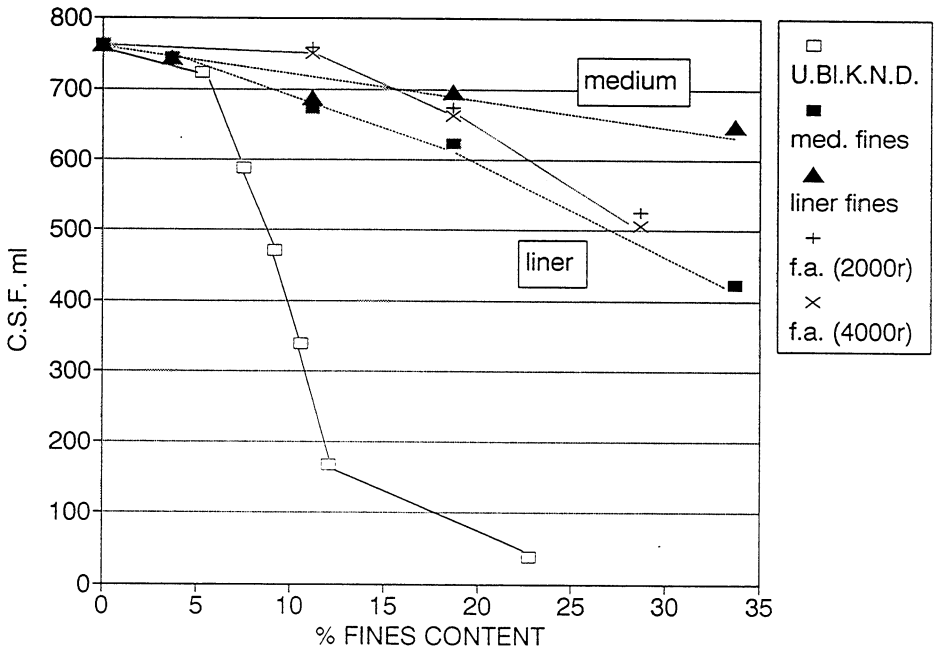

Figure 10. Variation of Canadian Standard Freeness with Fines Content Comparing Medium and Liner Fines Addition with Once Dried Fines Addition to a Never Dried Unrefined Unbleached Kraft Pulp.

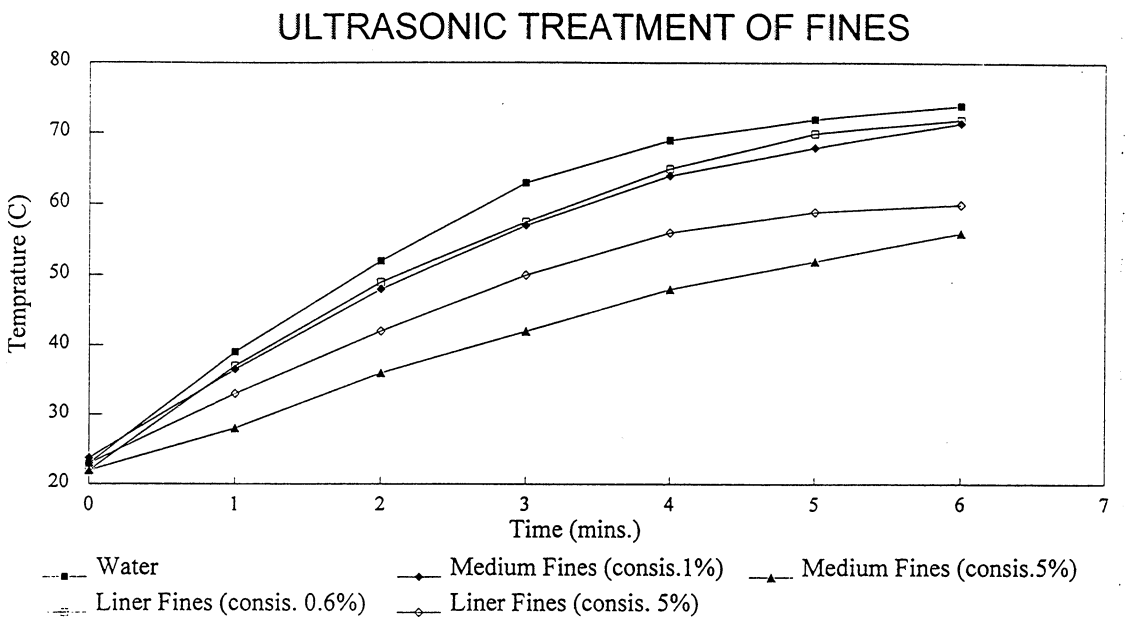

Figure 11. Temperature Rise with Time for Ultrasonic Treated Medium and Liner Fines at Various Consistencies.

MULTIPHASE FLOW IN RECYCLING OPERATIONS

STATUS REPORT

FOR

PROJECT F009-03

Ted Heindel

March 22 - 23, 1995

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

TECHNICAL PROGRAM REVIEW

Project Title: MULTIPHASE FLOW IN RECYCLING OPERATIONS
Project Code: DEINK
Project Number: 3681-04/F00903
Division: Engineering and Paper Materials
Project Staff: Ted Heindel
Project Budget: $74,917

OBJECTIVE

The objective of this project is to increase flotation efficiency by maximizing contaminant removal from waste paper while minimizing fiber loss. This objective will be realized by developing a better understanding of the fundamental processes involved in flotation separation.

SUMMARY

This report addresses the proposed research direction that will allow us to quantify the fundamental fluid mechanic processes important to flotation. It is assumed that in this phase of the study, the chemistry conditions are favorable for flotation. The report reviews the project goals for the present period, briefly summarizes the current flotation knowledge, outlines the specific project tasks, and then states the goals for the next period.

GOALS

Project goals for the past period (September 1994 to March 1995) involved:

1. To learn as much general information as possible about the pulp and paper industry, while focusing attention on current paper recycling technology.

   Status: Complete

   This goal was achieved through reading the current literature and, when possible, participating in mill visits. MacMillan-Bloedel's Pine Hill mill, Pine Hill, Alabama; Georgia-Pacific's Leaf River mill, New Augusta, Mississippi; and Champion International's mill, Cantonment,

Florida were visited in September in conjunction with the new graduate student orientation. Bowater's Southern Division mill, Calhoun, Tennessee, was visited in November, and Black Clawson's pilot facility, Middletown, Ohio was visited in November and December. Future site visits at other locations are also being planned when time permits.

INTRODUCTION

Flotation is a selective separation process that utilizes a gas carrier to raise suspended matter to the surface of a liquid. Particles that fall within a size range of 20 to 150 microns are typically affected by flotation (Ferguson, 1994), and these particles must be free to move throughout the suspension. Of these small, freely moving particles, only those that are hydrophobic (either naturally or chemically induced) attach to the gas bubbles and rise to the surface. Assuming these conditions are satisfied, the understanding and improvement of the fluid mechanics related to this separation process is the focus of this study.

The main objective of flotation is maximum contaminant removal and minimum fiber loss. Therefore, pulp brightness and optical cleanliness should increase when the flotation accepts are compared to the feedstock. Additionally, flotation should improve the runnability and printability of stock containing secondary fiber when compared to similar stock that has not undergone flotation.

Today, commercial flotation systems can remove between 90 and 95% of the contaminants that can possibly be removed by infinite flotation (called hyperflotation) (McCool, 1993). However, flotation processes were originally borrowed from the mineral separation industry and have, for the most part, relied on empirical methods for development within the pulp and paper industry. Additionally, many of the hydrodynamic effects of air bubbles in a pulp slurry and their influence on contaminant removal remain unknown.

Flotation Fundamentals

In a typical flotation unit used in the pulp and paper industry, the incoming stock to the unit has the following parameters: pH 8-9, consistency 0.8-1.2%, and temperature 40-45°C (Ferguson, 1994). McCool (1993) described many different parameters that influence flotation, and they can be divided into those that affect the contaminant (particle), the bubble, the mixing (interaction) between the two, and the overall process. These parameters are summarized in Table 1.

Table 1: Major parameters that affect flotation (McCool, 1993).

Particle	Quantity
	Size
	Shape
	Density
	Surface Chemistry
	Agglomeration
Bubble	Gas Carrier
	Quantity
	Size
	Surface Chemistry
	Injection Technique
Mixing (gas/particle interaction)	Nature
	Intensity
	Time
Process Conditions	Waste Paper Type
	Type and Amount of Ink
	Type and Amount of Ash
	Fiber Characteristics
	Consistency
	Temperature
	Retention Time
	Cell Geometry
	pH
	Chemical Environment

Typical flotation involves three distinct zones: mixing, coalescence, and separation. The mixing zone is where a fast moving fiber suspension stream is mixed with air to promote collisions and hydrophobic contaminant attachment to the air bubble. Residence time in the mixing zone is on the order of a few milliseconds, while total residency time in the flotation cell is much longer (Lindsay et al., 1994). In order for as many particles as possible to attach to the air bubbles in the mixing zone, the specific air bubble surface area, defined as the ratio of bubble surface area to bubble volume, must be as large as possible. Assuming spherical air bubbles, the air bubble diameter is inversely proportional to the specific surface area (Fig. 1). Therefore, the bubble diameter should be as small as possible for maximum contaminant removal. However, only bubbles with diameters larger than about 0.3 mm have sufficient buoyancy to push through the fibrous network in a pulp slurry. Typically, a bubble diameter of approximately 1.0 mm is assumed to be a realistic bubble size for flotation separation in a pulp slurry. Also, to accommodate a range of contaminant particle sizes, it is important that today's flotation cells generate a range of bubble sizes (Fallows, 1992).

Following mixing, the three-phase mixture enters the coalescence zone, where much less shear is present. The bubbles interact and coalesce, forming larger bubbles which have adequate buoyancy to rise through the fibrous network. Finally, there is the separation zone, where large bubbles (approximately 1 cm or greater) are present, and where the contaminant-laden froth is removed from the surface (Lindsay et al., 1994). These three zones are present in some form or another in each of the four types of modern flotation cells employed in the pulp and paper industry (rectangular, elliptical, cylindrical, or pressurized), which are supplied by six major equipment suppliers (Beloit, Bird-Escher Wyss, Black Clawson, Fiberprep-Lamort, Kamyr, and Voith) (McCool, 1993).

Selected Past Flotation Studies

Since flotation technology used in the pulp and paper industry was adopted from mineral flotation, Schulze (1991) employed mineral flotation fundamentals to summarize the theory of contaminant

attachment to bubbles. He determined the fundamental problems confronted in flotation within the pulp and paper industry were (1) the nonuniform, heterogeneous surface properties of contaminant particles with low weight and small size and (2) the high density of stock suspension where fibers form a quasi-elastic network. The most important microprocesses in flotation were also shown to be (1) the approach of a particle to a bubble in the flow field; (2) the formation of a thin liquid film, its rupture at a critical film thickness, and the development of the three-phase-contact; and (3) the stabilization of the aggregate against external stress forces. Schulze (1991) determined that the contaminant/bubble collision efficiency depended on the bubble and particle size, with the collision probability being higher for larger particle sizes and smaller bubble sizes. However, bubbles have to be sufficient to break through the fibrous network, and as a general rule, typical air bubble diameters are assumed to be on the order of 1 mm (Fallows, 1992).

Hou and Hui (1993) theoretically characterized flotation as a macroprocess composed of many microprocesses taking place globally at the same time, but locally in sequence. They summarized the forces on an ink particle in an air/fluid system by considering buoyancy, gravity, capillary forces, and other external dynamic stresses exerted on an ink particle/air bubble aggregate. The net force holding an ink particle to an air bubble was shown to be a complex function of the differential density, particle size, bubble size, contact angle, and the penetration distance of the particle into the air bubble. The capillary force was the most dominant force acting on the ink particle, and was strongly influenced by contact angle and the penetration distance of the particle into the air bubble. Penetration distance of the ink particles into the air bubble, immediately after the formation of three-phase-contact, was determined by the energies of collision. Contact angle was a complex function of the surface free energy of ink particles and liquid surface tension. The air bubble size influenced flotation mainly through its effect on collision efficiency. From this information, stability of the ink particle/air bubble aggregates was shown to be influenced by liquid surface tension, surface free energy of the ink particle, ink particle size, air bubble size, and the external turbulence.

Stratton (1992) also developed a simple theory describing the attachment force between a contaminant and an air bubble. He concluded that the attachment force was a function of bubble size, liquid surface tension, and the contaminant surface energy.

Lindsay and co-workers (Lindsay et al., 1994; Taylor et al., 1994; Taylor, 1993; George, 1994) used gamma densitometry to measure gas holdup in static and cocurrent air/water/pulp systems and hypothesized that preferential air channels existed in these systems under certain conditions. Lindsay et al. (1994) considered air rising through stagnant suspensions of recycled newsprint and cocurrent flow of air and pulp. Fibers were shown to promote bubble coalescence, and in stagnant suspensions, the fiber network also promoted air channeling. A fiber length analysis of the foam indicated that the froth preferentially removed long fibers.

This study was extended by Taylor et al. (1994), who studied the hydrodynamics of air/water/pulp slurry systems involving quiescent liquids as well as cocurrent flow. Using gamma densitometry, gas holdup (void fraction) was shown to be a critical parameter in bubble columns since a high void fraction implied a larger total interface area and/or longer bubble residence time in the pool. Generally, flow regimes in the cocurrent system resembled those in the quiescent system, and, compared to air/water systems, the fibers and flocs induced significant changes in the spatial distribution of air, in the bubble size distribution, and in the nature of the flow regime.

A recent Master's thesis at IPST (George, 1994) also involved the cocurrent multiphase system. George used a 1.5 m vertical test section that was 12.7 cm in diameter and varied the superficial air velocity over the range 0 to 4.2 cm/s and the superficial pulp slurry velocity between 2.5 and 7.1 cm/s. He employed repulped southern newsprint at consistencies between 0 and 2%. The flow system used a venturi air injector for bubble generation. At 1% pulp consistency, void volume increased over that observed for strictly an air-water system, and the gas holdup was higher near the column center than near the wall. The lateral void distribution was dependent upon bubble size, and, in general, smaller bubbles had a better distribution and preferably migrated toward the wall.

Walmsley (1992) experimentally studied static air/water/fiber and air/clove oil/fiber systems. Parametric variations included the geometry (cylindrical, 75 mm and 150 mm diameter; rectangular, 50 mm × 20 mm × 1500 mm), air orifice diameter (0.5 mm, 1 mm, 1.5 mm), water/fiber suspension type (bleached kraft pine, bleached kraft eucalyptus, and recycle yellow pages), column height-to-diameter ratios, and consistency (0 to 3.6%). The addition of 0.1% wood pulp to the water caused a significant change in bubble behavior. Both chemical and mechanical wood pulp fiber suspensions significantly decreased gas holdup at fiber concentrations beyond 0.6%. Reduced gas holdup implied bubble coalescence or channeling and a reduction in overall air/water interfacial area. In a flotation cell, this suggests a reduction in air/water interface area for contaminant attachment to the air bubble. Consequently, flotation efficiency was a strong function of fiber concentrations. If the fibers were present in a concentration high enough to mechanically entangle (flocculate), they appeared to decelerate the air bubble ascension and induced bubble coalescence. Also, a concern was raised that the increased frictional resistance of the interlocked fiber suspension could possibly loosen the fine particles attached to the air bubbles and prevent discharge. Finally, when the consistency was greater than 2%, bubble coalescence gave rise to channeling.

PLANNED WORK

This project assumes that the given chemistry is conducive to flotation separation and focuses on the following fundamental fluid mechanic issues in an air/water/pulp slurry:

A. multiphase flow regimes and structures

B. bubble dynamics

C. bubble/particle interactions

A better understanding of these fundamentals within the given multiphase system will improve the contaminant removal process, reduce fiber loss, and impact energy utilization. Specific tasks are summarized below.

Task A: Multiphase Flow Regimes and Structures

Both Lindsay and co-workers (Lindsay et al., 1994; Taylor et al., 1994; Taylor, 1993; George, 1994) and Walmsley (1992) determined that the presence of fibers has a considerable effect on the flow patterns within an air/fluid/pulp suspension. Task A will extend these initial studies to fully understand the effects various flow regimes and structures have on flotation within this complex multiphase system, and address flow regime modification and control techniques.

The initial work performed by Dr. Jeff Lindsay, using gamma densitometry, will be continued to determine the gas holdup in a cocurrent flow loop (Fig. 2) at consistencies of 0.8% and 1.2%. These studies are required because Walmsley (1992) stated that flotation efficiency was a strong function of fiber concentration. The proposed studies will determine if the previous conclusions obtained at consistencies of 1% (George, 1994) are applicable over the entire consistency range of typical flotation cells.

Methods to increase gas holdup and eliminate channeling, thereby increasing the bubble specific surface area, will also be investigated at consistencies of 0.8% and 1.2%. These procedures may include, but are not limited to, various flow modification techniques and flow agitation.

In addition to gamma densitometry, flash x-ray radiography will also be employed in the flow regime characterization and modification experiments. This technique will provide stop-motion visualization of the air/water/pulp suspension. The system, schematically represented in Fig. 3, consists of a Hewlett-Packard 150 keV flash x-ray, capable of providing a pulse of x-rays for 70 nanoseconds. The air/water/pulp slurry will absorb different amounts of radiation, due to density differences, and will be represented on film as different contrast levels. This technique will

photographically record the flow structures within this mixture. Comparisons with conclusions derived from the gamma densitometry measurements may also be possible.

Initial flash x-ray experiments will utilize the existing cylindrical channels currently available. However, future studies will include thin rectangular channels to obtained "two-dimensional" planar images that will aid in the identification and modification of channeling as well as bubble coalescence.

Information obtained from these experiments will be used to develop control techniques that will maintain desired flow conditions. For example, it may be determined that preferentially located baffles may be employed to promote mixing while eliminating channeling.

Task B: Bubble Dynamics

Controlling the air bubble size, quantity, ascension path, and coalescence in a pulp slurry is important for effective control of flotation separation. Most of the previous work in this area has been focused on mineral flotation (Schulze, 1983). Therefore, its extension to flotation in an air/water/pulp suspension is unknown. This task will study bubble dynamics and control in a pulp slurry.

Flash x-ray radiography will be used to record single bubbles in pulp suspensions by using injection techniques that produce a single string of bubbles. Parameters that affect bubble size distribution and control will be addressed, including air injection rate, shear rate, consistency, and surfactant concentration and type. Information from these experiments will be used to develop procedures to control the bubble size and distribution within an air/water/pulp suspension.

Task C: Bubble/Particle Interactions

Bubble/particle interactions address the hydrodynamic conditions necessary to bring a contaminant particle into contact with a bubble and the forces required for ultimate attachment. This task

initially confronts these issues on a theoretical basis. Extensions to experimental verification will be included when deemed appropriate.

Theoretical modeling of bubble hydrodynamics and bubble/particle interactions will be utilized to gain insight into the controlling factors that govern flotation at the contaminant particle level. Initial theoretical work derived from the mineral flotation industry (Schulze, 1983) will be extended to flotation deinking. Modifications to this theory to include deformable fibrous media may be required and will be addressed at that time. Information from these simplified models will be used to predict general trends and determine ideal theoretical conditions. Possible questions to be addressed include:

- What is the maximum particle size and/or weight a single air bubble of a given size can remove?
- Can the time required for collision between a contaminant and an air bubble be mathematically predicted?
- What role does the turbulence intensity play in bubble/particle interactions?
- What happens when a given bubble/particle combination interacts with another bubble or particle?

FUTURE GOALS (March 1995 to March 1996)

Goals for the next period include work under each of the tasks outlined above.

Task A: Multiphase Flow Regimes and Structures

1. Obtain gamma densitometry measurements in the cocurrent flow loop at pulp consistencies of 0.8% and 1.2%.

2. Modify the flow in the cocurrent flow loop by (a) baffles and (b) pulsed air injection to attempt to increase the gas holdup at fiber consistencies of 0.8% and 1.2%.

3. Visualize the structures within an air/water/pulp suspension using flash x-ray photography.

Task B: Bubble Dynamics

1. Use flash x-ray radiography to measure bubble size in an air/water/pulp mixture.

2. Compare bubble size distributions obtained in an air/water system with those from an air/water/pulp system.

Task C: Bubble/Particle Interactions

1. Determine the applicable theoretical models that can be extended from mineral flotation to flotation in a pulp suspension.

2. Determine those models derived for mineral flotation that are not applicable to flotation conditions within the pulp suspension and suggest possible improvements and/or modifications to these models that would extend them to air/water/pulp systems.

In addition to the goals established under each task, mill visits (when feasible) will be scheduled to observe the various recycling operations in action.

CONCLUSIONS

The objective of this project is to gain a fundamental understanding of the related fluid mechanic process variables that influence flotation, and how these variables can be controlled to improve contaminant removal. This report has summarized three specific task areas that are directed toward understanding the mechanics of flotation and will be undertaken over the next year.

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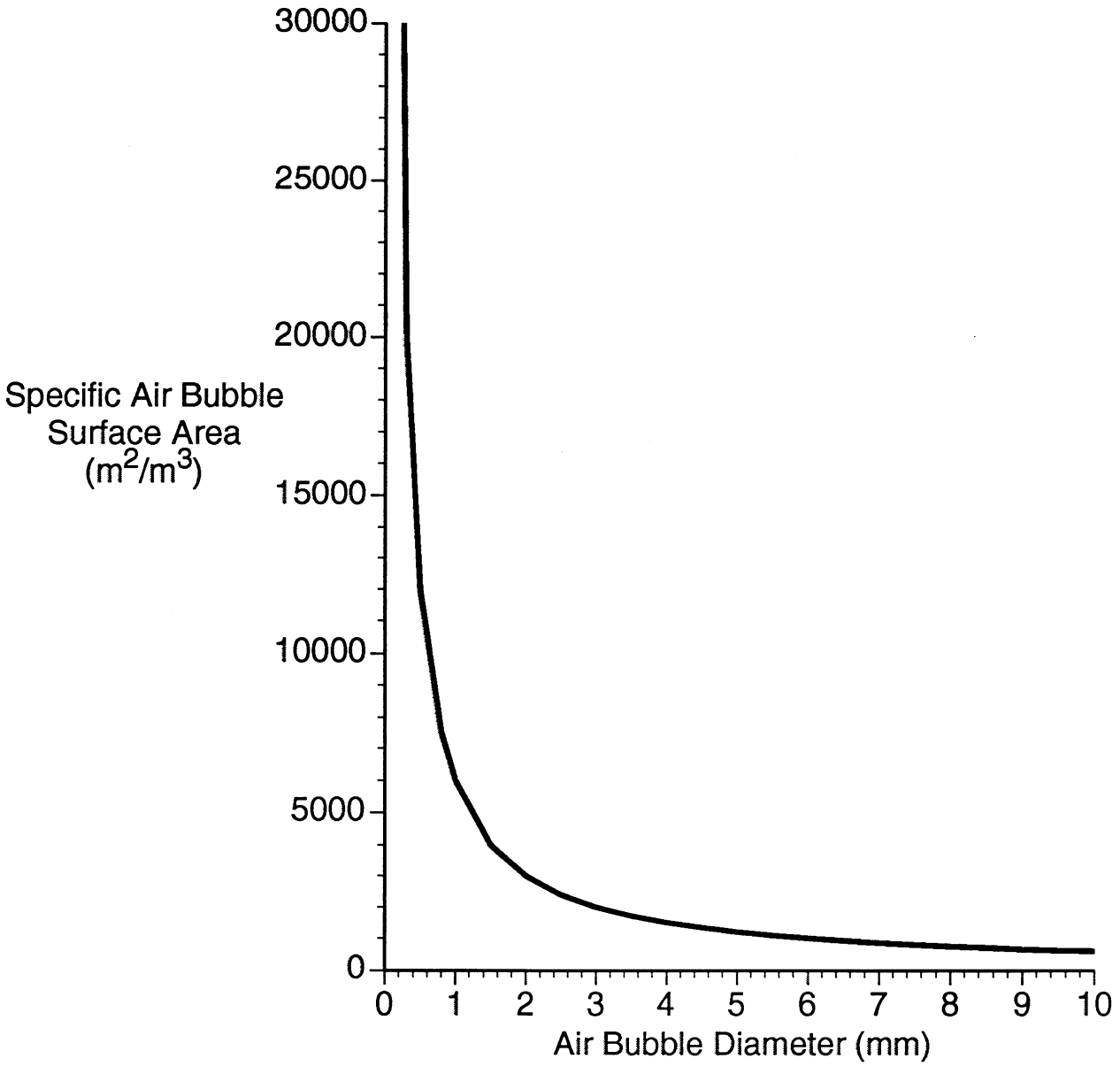

Figure 1: Specific air bubble surface area assuming a spherical air bubble.

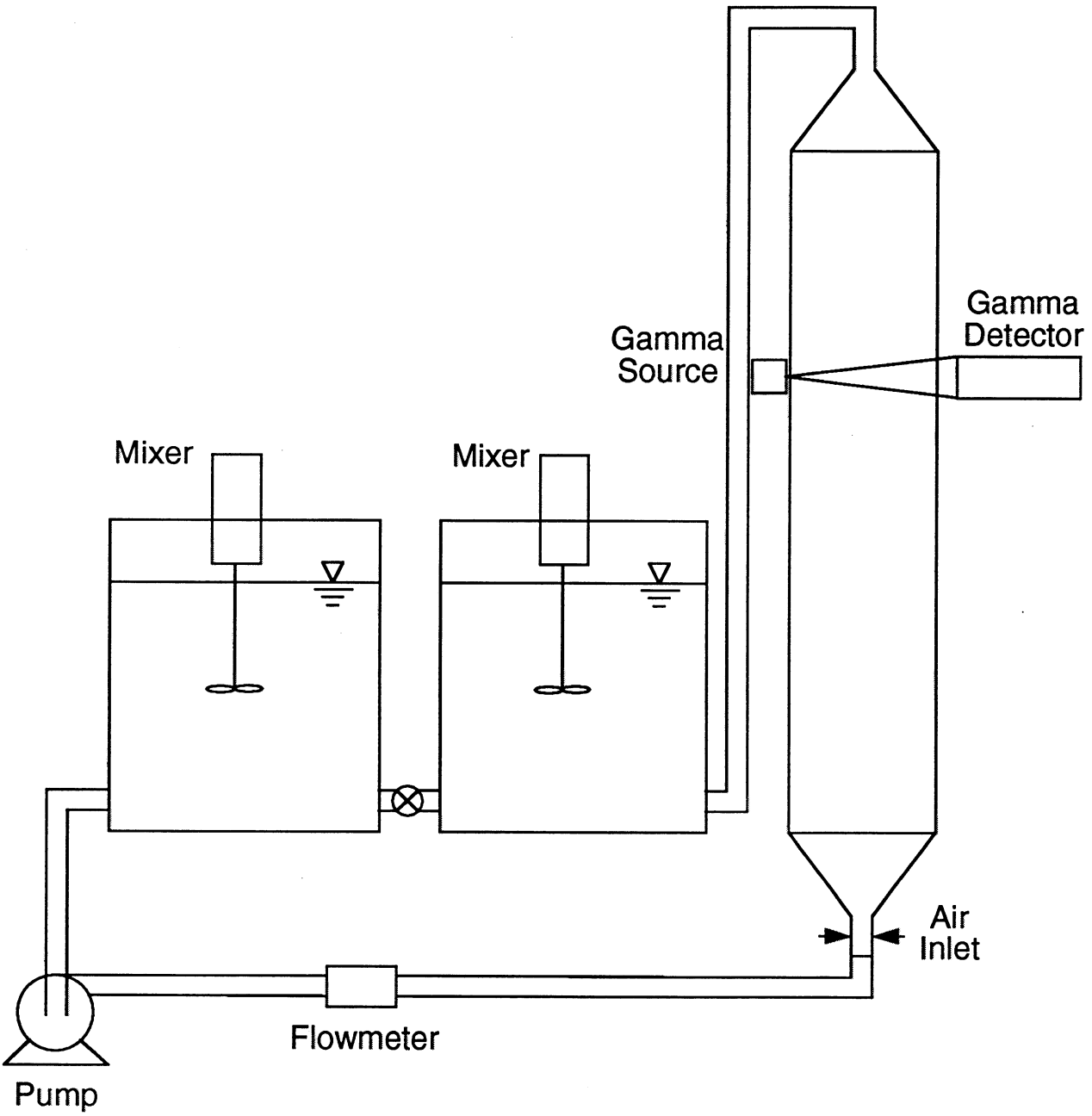

Figure 2: Schematic of the cocurrent flow loop.

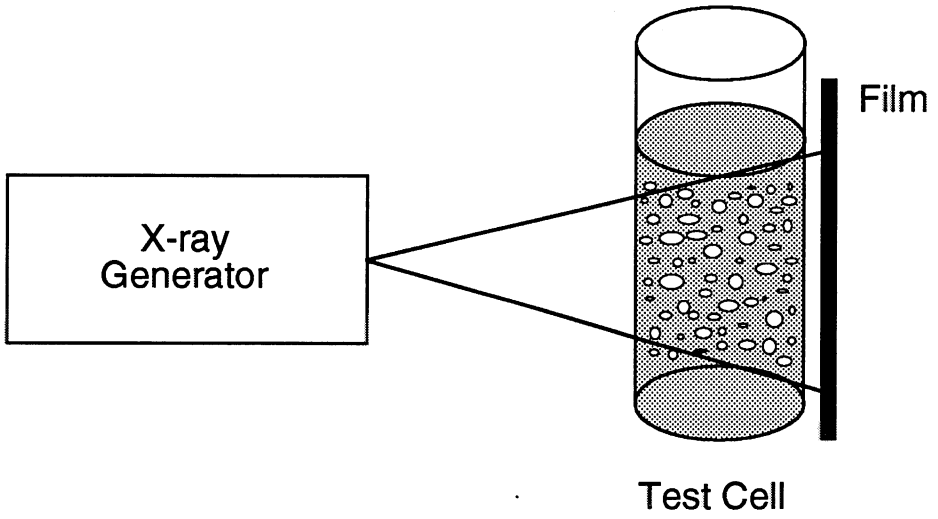

Figure 3: Schematic of the flash x-ray radiographic experimental setup.

STRENGTH PROPERTIES OF RECYCLED FIBERS AND PAPER

STATUS REPORT

FOR

PROJECT E001015

R. L. Ellis

March 22 - 23, 1995

Institute of Paper Science and Technology
500 10th Street, N.W.
Atlanta, Georgia

TECHNICAL PROGRAM REVIEW

Project Title:	Strength Properties of Recycled Fibers and Paper
Project Code:	RECYC
Project Number:	E00105
Division:	Engineering and Paper Materials
Project Staff:	R. L. Ellis
Project Budget:	

OBJECTIVE

Determine the principle factors contributing to the strength loss of recycled fibers and paper.

SUMMARY

A systematic procedure for identifying the principle factors contributing to the strength of recycled paper and fiber has been developed. This procedure relies on the Page Equation as the principle method for experimental design and data analysis. We have shown that the development of relative bonded area is a deficient property of recycled fibers We have eliminated fiber strength, fiber to fiber bonding, and fiber length, perimeter and coarseness as factors.

The principle papermaking tool used to develop relative bonded area is refining. Our experiments support the conclusions of earlier work done at IPST that refining will not develop the relative bonded area in recycled fiber at the same freeness of a never dried fiber.

We believe that increasing the acid group content of recycled fibers will improve the development of the relative bonded area. This report is an analysis of the contribution of acid groups to the strength of cotton fibers. We show that acid groups improve the

development of the relative bonded area. We propose experiments to study this effect in recycled wood fibers.

GOAL FOR 1994

Prepare a summary report: Complete.

GOAL FOR 1995

Quantify the effect of increasing acid group content on the properties of recycled wood fibers.

REPORT

The Effect of Acid Group Content on the Properties of Cotton Fibers

Prepared by D.L. Barzyk and R.L. Ellis

INTRODUCTION

Recycling, and the use of recycled fibers, is an ever-expanding concern of today's papermaker. The American Forest & Paper Association has identified recycling as a research priority for the industry; a fundamental understanding of fiber bonding was cited as a specific area requiring research (1). The Page Equation (2) can be used to separate fiber bonding into its components of specific bond strength and relative bonded area (RBA). Ellis and Sedlachek (3) used the Page Equation and reported that the loss of strength with recycling is due to a loss of bonded area. Ellis and Myers (4) have demonstrated that recycled fibers cannot regain their full papermaking potential through refining alone and that a more aggressive approach is required. The results of Ellis and co-workers, when coupled with a reevaluation of historic data presented here, suggest a novel method of upgrading the strength of recycled papers.

It has been established that carboxymethyl substitution enhances the strength of both cotton and wood pulps (5-8). The improved strength was attributed to increased plasticity of the fibers, increased bonding, increased bonded area, or increased aggregate

bond strength (5, 6). The analysis presented here indicates that the increase in strength was due to an increase in RBA. This result is expected from Scallan's explanation of the role of acidic groups on fiber swelling (9). Counter ions to acidic groups in fibers control the osmotic pressure and cause the fibers to swell. Scallan's explanation is bolstered by Talwar (6) who found that the strength increase with carboxymethylation was realized only when the acidic groups were deprotonated. Increased acidic group content can thus increase RBA. The controlled introduction of acidic groups into recycled fibers can therefore represent a method to upgrade the strength of recycled papers.

Numerous methods exist to introduce acidic groups on cellulose. These include direct oxidation of cellulose with nitrogen dioxide, ozone, hydrogen peroxide, and oxygen among others (10). Addition of sulfonic acid groups to lignin (11), the grafting of carboxylic acids to cellulose (5), and the formation of free radicals with devices such as electron beams (12) represent other pathways.

DATA ANALYSIS

Ellis and Sedlachek (3) have shown how to use the Page Equation to separate the factors which contribute to the strength of papers made with recycled fiber. The Page Equation is:

$$1/T = 9/8Z + (12gC/PLbRBA) \qquad (1)$$

where

T	= tensile breaking length
Z	= zero span breaking length
C	= fiber coarseness
P	= fiber perimeter
L	= fiber length
b	= fiber-fiber bond strength
RBA	= relative bonded area
g	= gravitational constant

RBA can be calculated from the scattering coefficients of the sheets.

$$RBA = (S_0 - S)/S_0 \qquad (2)$$

where

S_0 = scattering coefficient of unbonded sheet
S = scattering coefficient of paper sheet

Substituting Equation 2 into Equation 1 and rearranging produces an equation relating the tensile properties of the sheet to scattering coefficients.

$$[1/T - 9/8Z]^{-1} = b/\gamma - (b/\gamma S_0)S \qquad (3)$$

where

Page Parameter $= [1/T - 9/8Z]^{-1}$
$\gamma = 12gC/PL$

Equation 3 shows that the scattering coefficient of an unbonded sheet (used to calculate RBA) and the specific bond strength can be determined from readily measured quantities.

ANALYSIS OF EXPERIMENTAL RESULTS

Walecka developed a procedure and produced carboxymethyl cellulose by substituting cellulose hydroxyls with chloroacetic acid. Walecka performed several beater curves on these pulps and recorded strength data (5,13). The data collected by Walecka were re-evaluated using Equation 3. Walecka's data were suitable for this analysis with the exception that TAPPI opacity was recorded, not scattering coefficient. However, Talwar (6) followed Walecka and used the same pulp and techniques. Talwar's data (14) showed that degree of carboxymethyl substitution (D.S.) did not alter the reflectivity of the sheets. It was judged acceptable to use Talwar's reflectivity to determine scattering coefficients from Walecka's TAPPI opacities using a suitable table (15).

Figure 1 shows the relationship between freeness and breaking length for pulps studied by Walecka. He concluded that acid treatment increases the breaking length . We tested the results shown in Figure 1 by fitting the data to a model containing linear and quadratic terms in freeness and acid content. The statistics showed that the acid content was significant at the 95% confidence level. The R^2 for the regression was 0.96, and although this is a very large value of R^2, a better model can be developed, and we intend to develop the model in a later report. We used the quadratic fits to generate the cross plot shown in Figure 2. This plot shows the effect of acid content on tensile strength at a freeness of 500 ml. The tensile strength is improved by 44% over the range of acid contents studied. The maximum effect appears to be at an acid content of 2×10^{-4} mol acid/gram cellulose.

Since the purpose of this analysis is to understand how the acid content improves the tensile strength, in the context of Equation 1, we must explore the effect of acid content on each of the terms of the page equation. The effect of acid content on zero span tensile strength is shown in Figure 3. The data are scattered, but there is a general upward trend with increasing acid content. This trend can be seen in the plot shown in Figure 4. Since the data are scattered, we will use the measured values of zero span in the Page Equation. Although Walecka did not measure fiber lengths, the pulps were fractionated on a Bauer-McNett, and we were able to use these results to estimate fiber length (16). The effect of acid content on fiber length is shown in Figure 5. Increases in the acid content countered the impact of refining on fiber length reduction. The fiber length results are scattered; therefore, we will not attempt to smooth the data before inserting it in the Page analysis.

We plotted the reciprocal of L*[1/T - 9/8Z] versus scattering coefficient and the result is shown in Figure 6. Equation 3 predicts that this plot will be a single straight line if the data can be represented by the same fiber-fiber specific bond strength and the same specific scattering coefficient. The fit in Figure 5 is a straight line with an R^2 of 0.77. We tested the data shown in Figure 6 for dependency on acid content and found that this factor was not significant at the 95% confidence interval. We conclude that the Page

analysis has accounted for the observed effect of acid content. Since the fiber to fiber bond strength is equivalent for all the levels of acid content, we conclude that the principle effect of acid content is to increase the relative bonded area at any level of refining.

Since zero span breaking length, fiber length, and RBA all change with acid content, it is instructive to calculate to relative contributions of these to the observed rise in breaking length. The maximum beneficial effects of acid groups appears to occur at a level of around 2×10^{-4} mol acid/gram cellulose. This acid content was then compared to the control pulp for calculation of relative contributions. The values for breaking length, zero span breaking length, fiber length, and RBA at 500 freeness were inserted into Equation 1 to establish a value for the unknown quantities. The known values were then inserted into Equation 1 and varied one at a time from low to high levels to determine the relative contribution of each quantity. The increase in breaking length from low to high acid content was +30%. The relative contribution of zero span breaking length to this change in breaking length was calculated to be 9%, fiber length being 20%, and RBA representing 71%.

The result of this analysis suggests that the inclusion of acid groups into recycled pulp is a method to improve the general strength characteristics of these pulps. The central question that remains is the efficiency of introducing acid groups into recycled pulps.

DISCUSSION/CONCLUSIONS

This analysis of historical data demonstrates that introduction of carboxylate groups in fibers increases the relative bonded area. We believe the mechanism of this effect is an increased conformability of the fibers due to increased fiber swelling. Introduction of acidic groups into recycled fibers, from direct oxidation or grafting, appears to offer a path to upgrade the strength of recycled papers.

There are many chemical treatments which can introduce acid groups into wood pulp. From a practical point of view, ozone and hydrogen peroxide offer the best opportunity to introduce acid groups in fully bleached pulps. These chemicals are already being employed in the bleaching of recycled fibers. Therefore, experiments to establish the optimum conditions for direct oxidation of the fiber cellulose will be important to the design and operation of bleaching operations. We intend to pursue work in this area of research. Although ozone and peroxide will introduce acid groups into unbleached pulps, another method is possible. The introduction of sulfonic acid groups may eliminate the yield loss expected from other treatments. We intend to investigate the possibility that sulfonation of unbleached pulps will improve strength characteristics.

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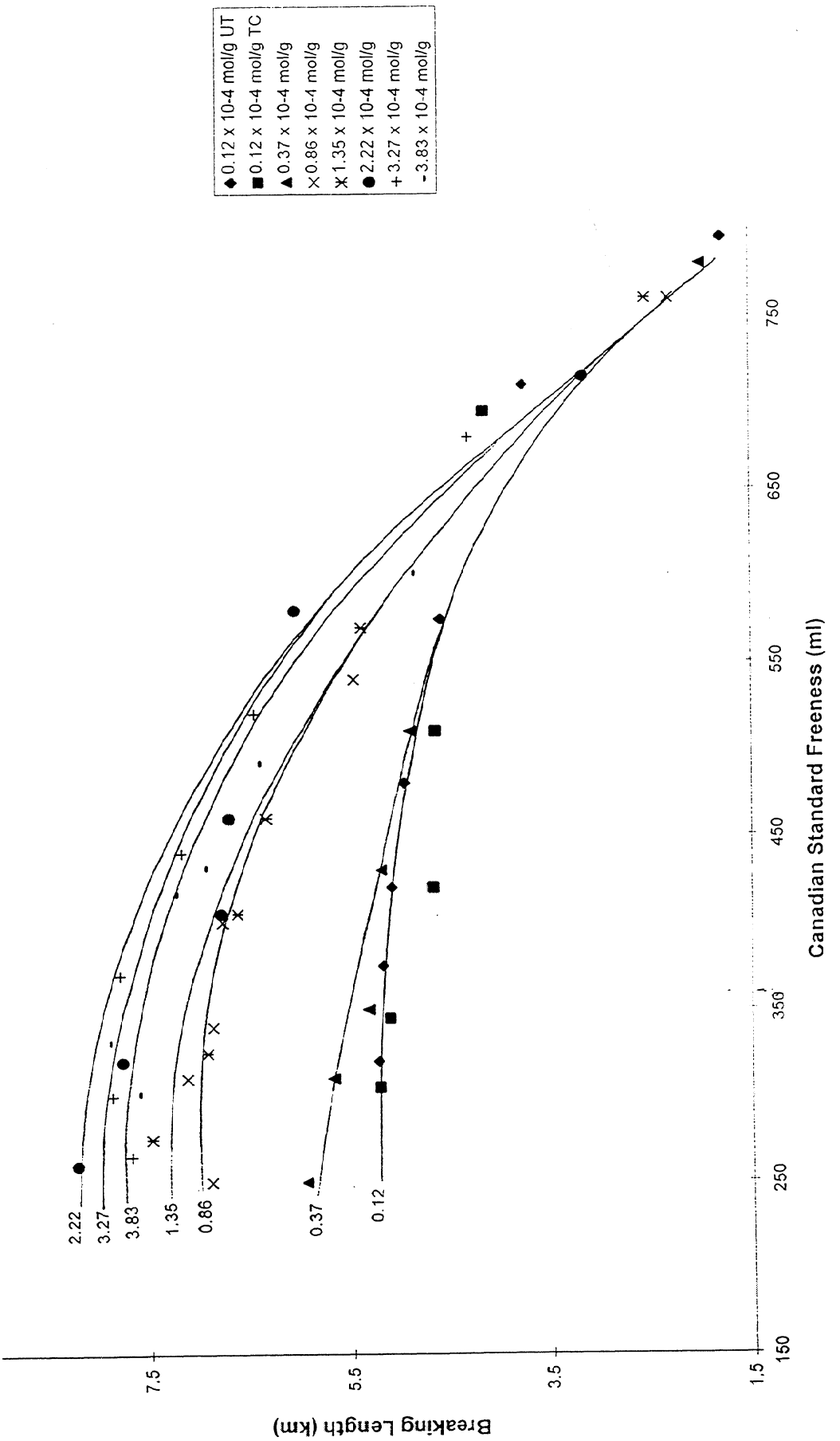


FIGURE 1. The effect of refining and acid content on tensile strength.

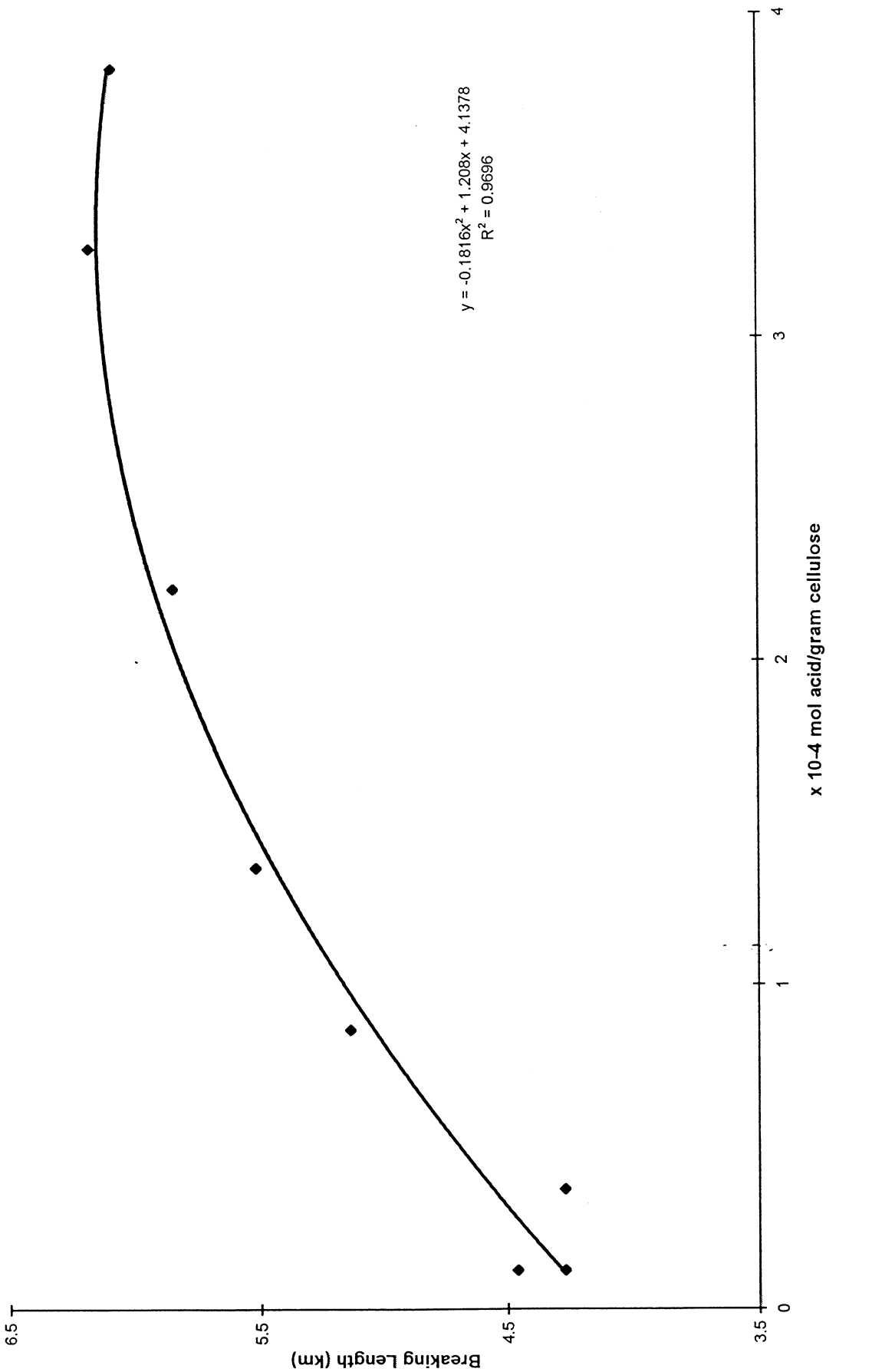


FIGURE 2. The effect of acid content on breaking length at 500 Canadian Standard Freeness.

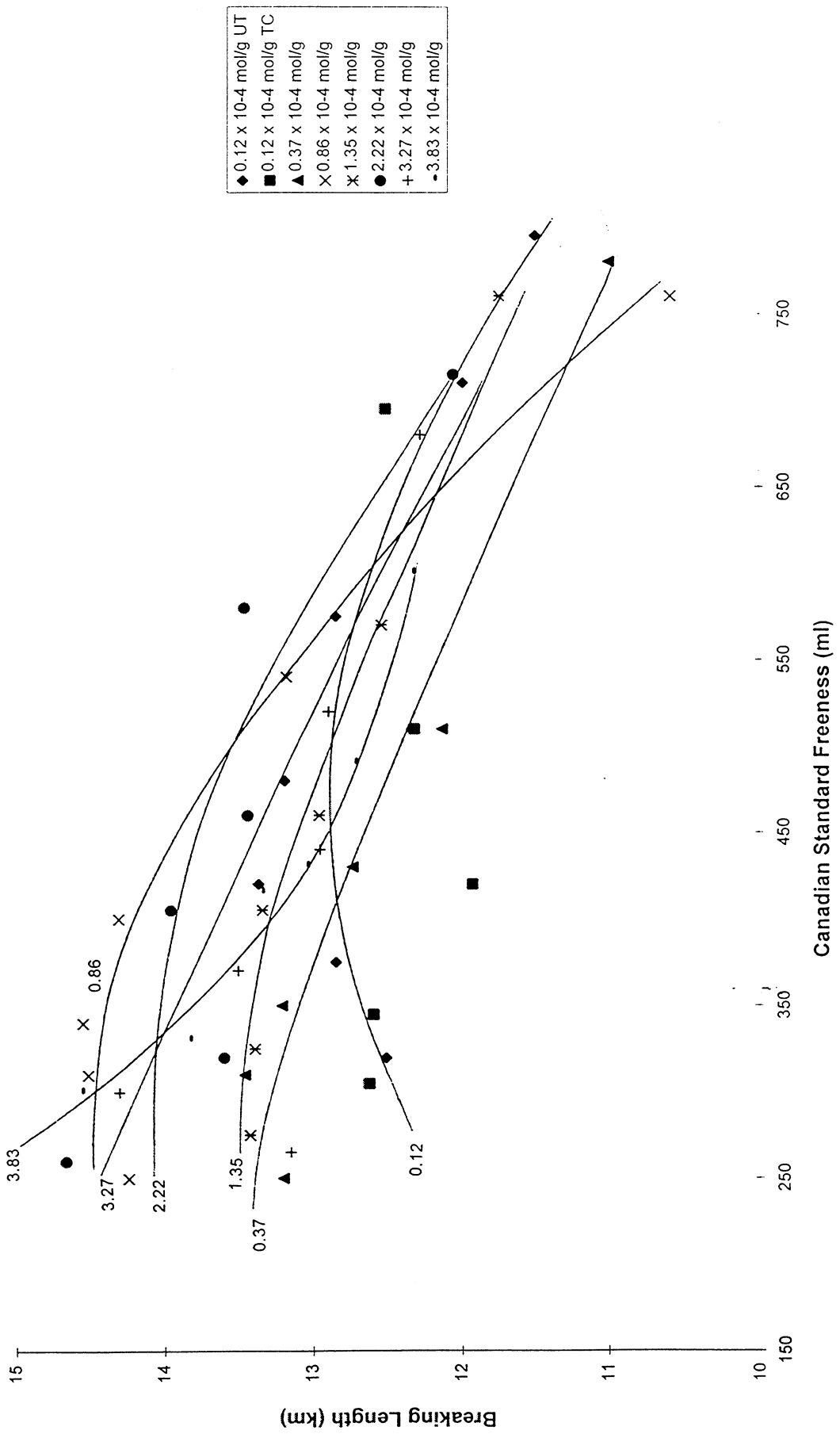
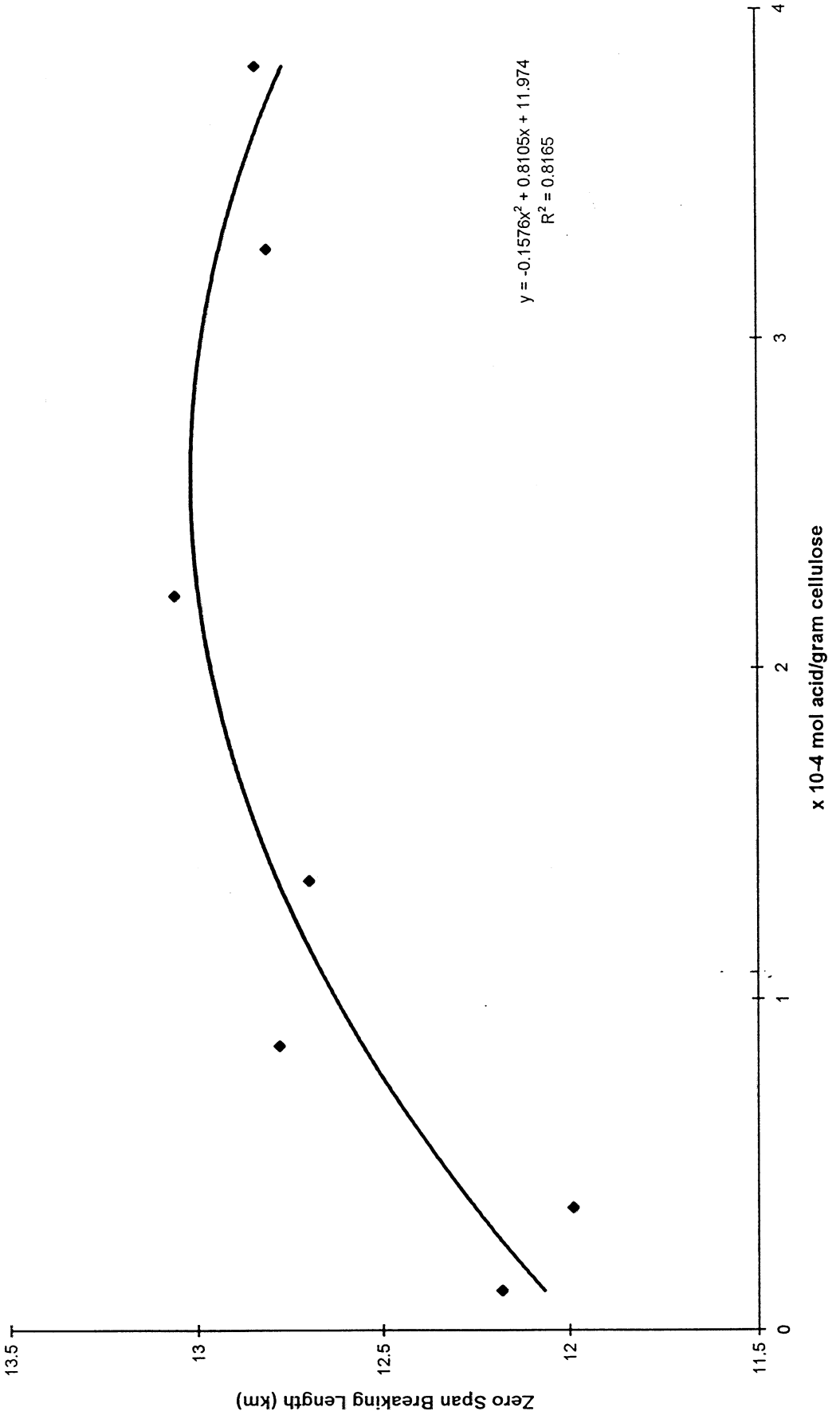


FIGURE 3. The effect of refining and acid content on zero span tensile strength.

FIGURE 4. The effect of acid content on zero span breaking length at 500 Canadian Standard Freeness.



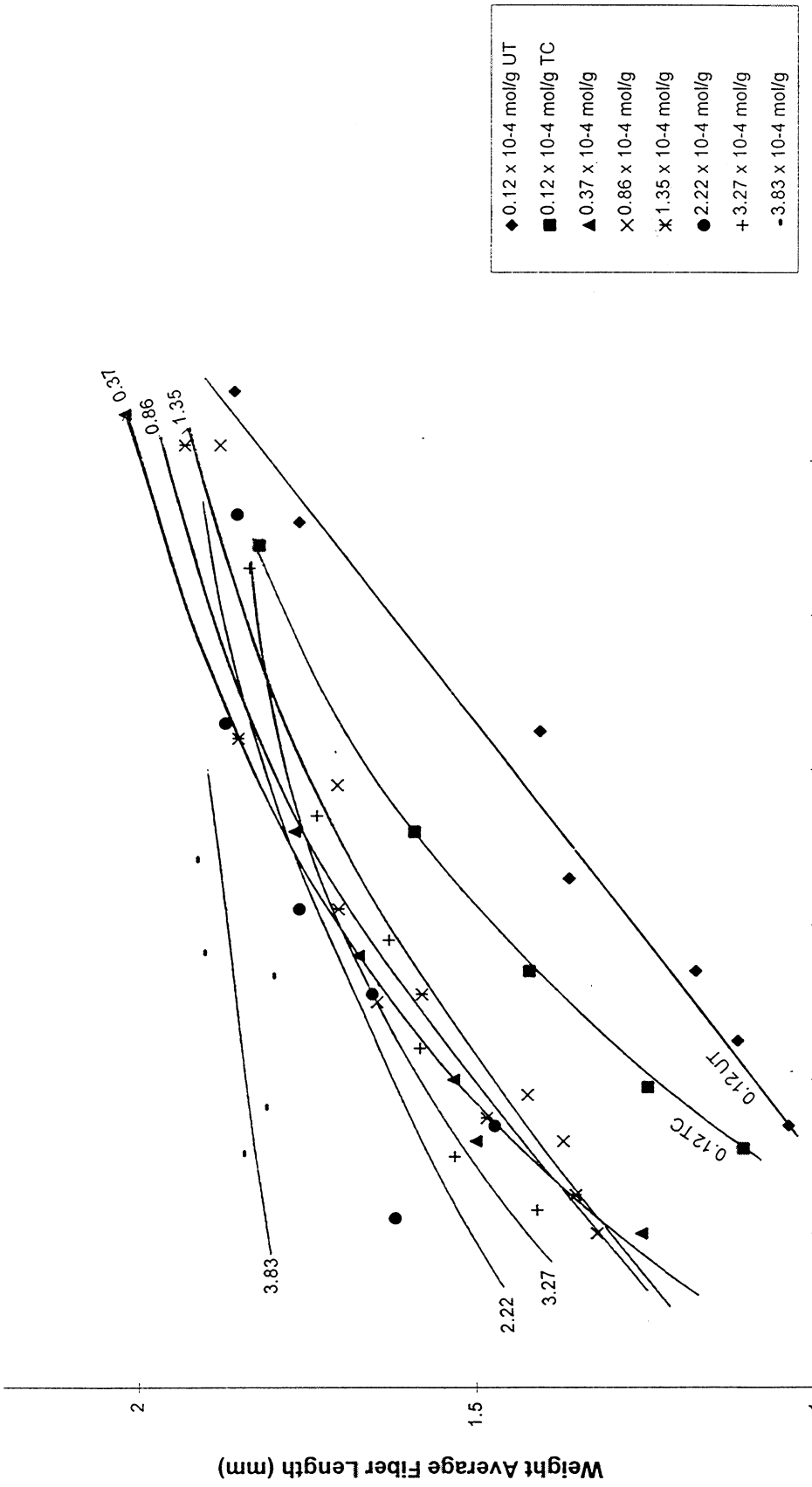


FIGURE 5. The effect of refining and acid content on fiber length.

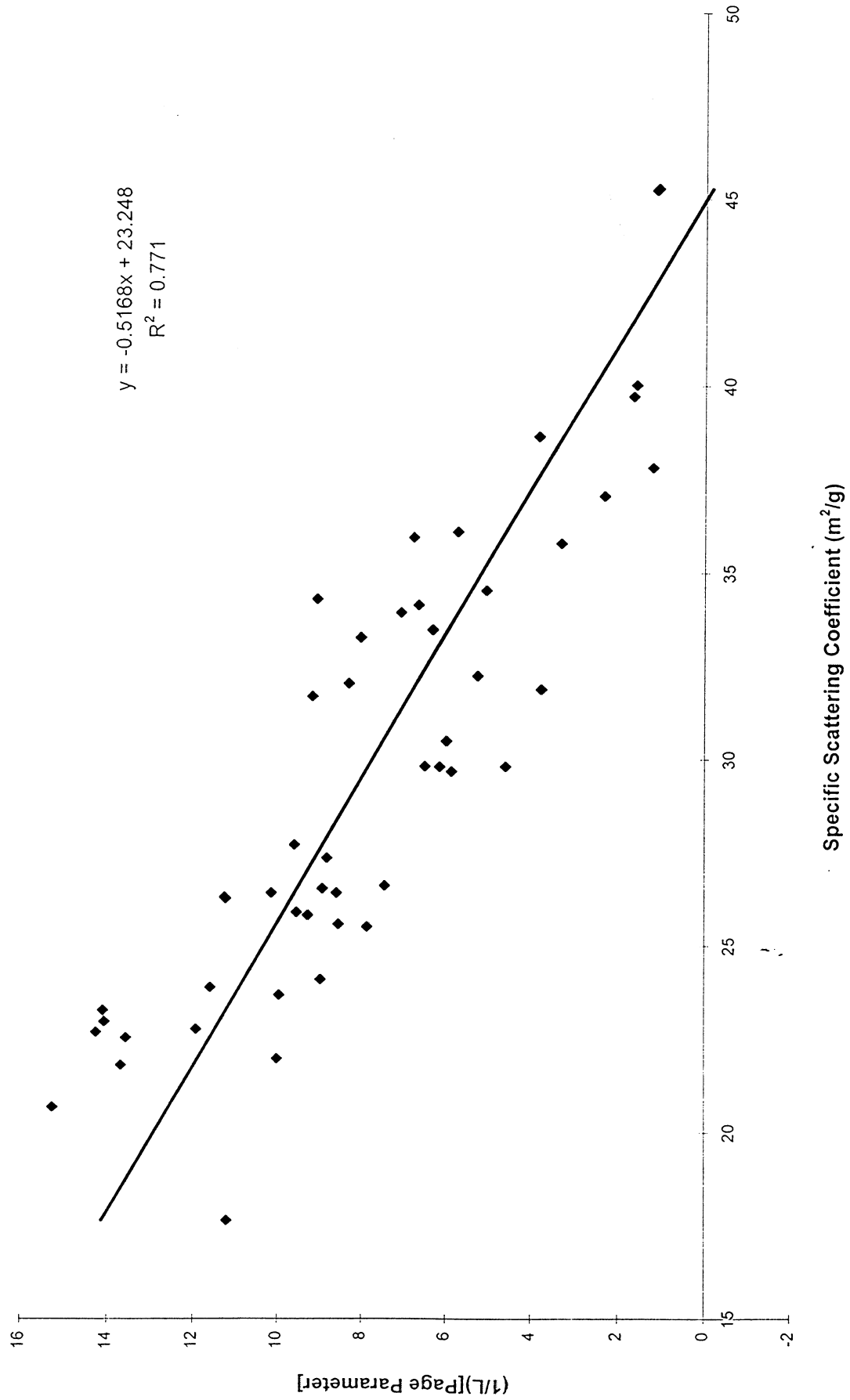


FIGURE 6. Page plot for entire range of acid contents and refining.